Field Investigation Report for Waste Management Area S-SX

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FIELD INVESTIGATION REPORT FOR WASTE MANAGEMENT AREA S-SX

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Abstract: This field investigation report for WMA S-SX addresses the
results and modeling efforts from field investigation over the last
three years (1997 through 2000).

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EXECUTIVE SUMMARY

This *Field Investigation Report for Waste Management Area S-SX* presents the most recent comprehensive assessment of existing and new information to clarify the current understanding of the nature and extent of past releases in the S and SX tank farms that comprise waste management area (WMA) S-SX. This report evaluates the potential of corrective actions to reduce or eliminate the consequences of these past releases on human health and the environment. This report presents the results of the most thorough field investigation ever conducted on the impacts associated with tank leaks from S and SX farm single-shell tanks. Also presented are computer simulation results of future groundwater impacts from such past releases, as well as a risk assessment. The *Resource Conservation and Recovery Act of 1976* (RCRA) Corrective Action Program and its implementing regulations require a rigorous investigative process to maintain a high degree of technical integrity and usefulness to decision makers. This task included the integrated efforts of the Tank Farm Vadose Zone Project; other U.S. Department of Energy (DOE), Office of River Protection (ORP) tasks; the Hanford Groundwater Vadose Zone Integration Project; Hanford Groundwater Program; and National Laboratories and universities funded from DOE Headquarters.

This *Field Investigation Report for Waste Management Area S-SX* was mandated by the RCRA Corrective Action Process, as documented in *Phase I RCRA Facility Investigation Corrective Measures Study Work Plan for Single-Shell Tank Waste Management Areas*.¹ That work plan provides the overall framework to guide groundwater and vadose zone investigation and decision making for single-shell tank WMAs at the Hanford Site. The approved *Hanford Federal Facility Agreement and Consent Order*² (HFFACO a.k.a. Tri-Party Agreement) Change Package M-45-98-03 establishes that this field investigation report is to support the development and implementation of interim measures and interim corrective measures and support single-shell tank waste retrieval and closure activities through integration with other projects (e.g., Hanford Groundwater/Vadose Zone Integration, Single-Shell Tank Retrieval).

Major conclusions of this report follow.

- Waste from tanks in the SX tank farm has impacted groundwater most likely due to enhanced contaminant transport caused by nearby waterline leaks, with technetium-99 groundwater concentrations reaching over 80,000 pCi/L. The drinking water standard³ for technetium-99 is 900 pCi/L.

¹ DOE-RL, 2000, *Phase I RCRA Facility Investigation Corrective Measures Study Work Plan for Single-Shell Tank Waste Management Areas*, DOE/RL-99-36, Rev. 1, U.S. Department of Energy, Richland Operations Office, Richland, Washington,

² Ecology, EPA, and DOE, 1989, *Hanford Federal Facility Agreement and Consent Order*, as amended, Washington State Department of Ecology, U.S. Environmental Protection Agency, and U.S. Department of Energy, Olympia, Washington.

³ 40 CFR 141, "National Primary Drinking Water Regulations," *Code of Federal Regulations*, as amended.

- Waste from WMA S-SX is projected to significantly impact groundwater in the future, resulting in a projected maximum incremental lifetime cancer risk of 0.01 for an industrial worker near the tank farm boundary. This is a theoretical calculation for an industrial worker consuming 2 L of water a day from a groundwater well at the tank farm boundary.
- Predictions of future contaminant behavior and groundwater impact are most sensitive to estimates of total inventory and recharge.
- Control of moisture movement through the tank farms soils presents the greatest opportunity to minimize future impacts on groundwater resources.
- The geochemistry associated with the movement of cesium-137 from tank leaks in WMA S-SX has been understood, thus providing an explanation of the depth of cesium-137 contamination associated with these tank leaks. Significant additional movement of cesium-137 is not expected.
- The field, laboratory, and computational results associated with this effort have strengthened the support for conceptual models on moisture flow and contaminant transport and provide an improved understanding of contaminant profiles in highly impacted regions of the WMA S-SX tank farm vadose zone.
- The fine-grained sediments associated with the undifferentiated Hanford formation/Plio-Pleistocene unit have retarded migration of many of the contaminants released from the tanks.
- Interim measures have been identified and completed in WMA S-SX that are expected to significantly reduce future consequences.
- Drilling technology advancements developed under this project have resulted in improved sample quality and reduced costs over past drilling efforts in highly radiologically contaminated areas.

Recommendations in this report address interim measures, accelerated corrective measures, future tank operations, collection of additional WMA S-SX data and information, lessons learned, and restructuring of the RCRA Corrective Actions Program schedule.

Key recommendations are the following.

- The interim measures (waterline isolation and leak testing, runoff controls, groundwater remediation) should be extended to other tank farms. Periodic waterline testing should be conducted.
- An engineering study is required to determine the costs and impacts of placing an interim surface barrier to determine the impact to tank farm operations and planned waste retrieval actions.
- Aboveground piping should be used whenever possible for improved leak detection.

- Future liquid waste retrieval activities should evaluate the use of either limited water-based or dry waste retrieval methods instead of Supernate where significant cesium-137 exists in soils.
- A limited number of additional characterization activities that may be useful in making long-term remedial action decisions have been identified. Additional data collection is warranted only if the data collected are anticipated to have a significant impact on the findings presented in this report. Additional data are not necessary to support interim action decisions.

The following sections provide further details and support:

- Section 1.0. Introduction
- Section 2.0. Investigative Approach
- Section 3.0. Investigative Results and Conclusions
- Section 4.0. *Summary* and Conclusions of the Impact (Risk) Evaluations
- Section 5.0. Conclusions
- Section 6.0. Recommendations.

Section 1.0, Introduction and Section 2.0, Investigative Approach

Twelve 23-m (75-ft) diameter underground tanks in the S tank farm and 15 similar tanks in the SX tank farm have stored hazardous, high-level radioactive mixed wastes for several decades. These tanks, along with their associated infrastructure for WMA S-SX, are located in the 200 West Area of the Hanford Site (Figure ES.1). This WMA was placed in RCRA groundwater monitoring assessment because of elevated specific conductance and high-levels of technetium-99 in downgradient monitoring wells. Based on the groundwater impacts at WMA S-SX and similar determinations for other SST farm releases, DOE established the RCRA Corrective Action Program to characterize the vadose zone and groundwater; to perform analyses to aid in the understanding of contaminant fate, moisture movement, and contaminant transport; and to estimate future environmental impacts from past leaks.

The framework for the investigative approach for the RCRA Corrective Action Program was developed through negotiations with the Washington State Department of Ecology and DOE in *Hanford Federal Facility Agreement and Consent Order* Change Package M-45-98-03. The RCRA facility investigation/corrective measures study work plan⁴ encompasses the aspects of work common to all WMAs and establishes the regulatory and programmatic framework for the overall RCRA Corrective Action Program.

⁴ Caggiano, J.A. 1996, *Groundwater Water Quality Assessment Monitoring Plan for Single-Shell Tank Waste Management Area S-SX*, WHC-SD-EN-AP-191, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Figure ES.1. Location Map of Single-Shell Tank Waste Management Area S-SX and Surrounding Facilities in the 200 West Area

To ensure appropriate data were collected to meet the needs for field investigation reports as identified in site-specific work plans, an implementation plan was prepared as Appendix J of the RCRA facility investigation/corrective measures study work plan.¹ Key to the implementation plan approach is first understanding what efforts would be most appropriate for a field investigation report and then addressing assimilation of data necessary to complete those evaluations. As documented in the Appendix J implementation plan, the key evaluation for assessing effectiveness of interim measures and the need for additional data is that of the potential risk to a human receptor.

The effort for WMA S-SX included collecting and analyzing available information, identifying data gaps, and planning future field characterization activities. The extensive available information is summarized in *A Summary and Evaluation of Hanford Site Tank Farm Subsurface Contamination*⁵ and in *Subsurface Physical Conditions Description of the S-SX Waste Management Area*.⁶ This information was used in a set of data quality objectives processes to determine data gaps. Data gaps were filled under two field programs documented in *Preliminary Site-Specific SST Phase 1 RFI/CMS Work Plan Addendum for WMA S-SX*⁷ and *Site-Specific SST Phase 1 RFI/CMS Work Plan Addendum for WMA S-SX*.⁸ These work plan addenda were approved by DOE and the Washington State Department of Ecology. Other work, particularly that of the national laboratories and universities funded by DOE headquarters, is in addition to and complements the work presented in the work plan addenda.

Section 3.0, Investigative Results and Conclusions

Much new data were collected as part of the total WMA S-SX characterization effort. This discussion is divided into three main sections:

- Field activities, which involves the collection of soil samples and geophysical measurements
- Laboratory analyses of those soil samples
- Data evaluations of these measures and analyses as well as numerical simulations of past events.

⁵ Jones, T.E., R. Khaleel, D.A. Myers, J.W. Shade, and M.I. Wood, 1998, *A Summary and Evaluation of Hanford Site Tank Farm Subsurface Contamination*, HNF-7603, Rev. 0, Lockheed Martin Hanford Corporation, Richland, Washington.

⁶ Johnson, V.G., T.E. Jones, S.P. Reidel, and M.I. Wood, 1999, *Subsurface Physical Conditions Description of the S-SX Waste Management Area*, HNF-4936, Fluor Daniel Hanford, Incorporated, Richland, Washington.

⁷ Henderson, J.C., 1999, *Preliminary Site-Specific SST Phase 1 RFI/CMS Work Plan Addendum for WMA S-SX*, HNF-4380, Rev. 1B, Fluor Daniel Hanford, Incorporated, Richland, Washington.

⁸ Rogers, P.M. and A.J. Knepp, 2000, *Site-Specific SST Phase 1 RFI/CMS Work Plan Addendum for WMA S-SX*, HNF-5085, Rev. 1, CH2M Hill Hanford Group, Incorporated, Richland, Washington.

Field Activities. Major field investigations defined in the work plans were conducted at the following locations (see Figure ES.2):

- Installation of a RCRA-compliant groundwater well (299-W23-19) southwest of tank **SX-115**
- Sediment sampling and decommissioning of borehole **41-09-39** (well 299-W23-234)
- Collection of vadose zone characterization data from the installation of three RCRA groundwater monitoring wells (299-W23-48, -49, and -50)
- Installation of an exploratory slant borehole (299-W23-64) beneath tank **SX-108**
- Shallow vadose zone soil investigation around tank **S-104**.

For each of the boreholes drilled, soil samples were retrieved for laboratory analyses and geophysical logging was performed. In each of these boreholes, gamma logging (to measure the concentration of gamma-emitting radionuclides) and neutron logging (to measure moisture content) were performed. In addition, thermal logging (to measure the temperature of the borehole casing and hence the soil temperature) was performed on borehole **41-09-39** and the **SX-108** slant borehole. Finally, neutron activation measurements were done on borehole **299-W23-19** to determine concentrations of certain nuclides. The shallow soil investigation performed gamma logging and limited soil collection.

Additional geophysical logging was performed in existing boreholes within **WMA S-SX**. To supplement earlier gamma-logging work, boreholes with high gamma radiation were relogged with a high-rate detector to quantify the highest concentrations of cesium-137 contamination. Such information was used in the determination of the amount and extent of this radionuclide. In addition, neutron logging was performed on most of the existing boreholes in the south end of the **SX** tank farm.

The major field characterization accomplishments included the following.

- Improvements in drilling technology allowed safe and efficient sample collection of contaminants in the high radiation zone beneath tank **SX-108**. Other improvements aided the program in a variety of areas.
- Use of the specially developed sampler is an effective means for sample collection in high radiologically contaminated areas.
- Air rotary drilling can be performed in the tank farms but is not cost effective due to the high cost of contamination confinement and associated air release risk to the environment.
- The distribution of moisture content, on the basis of drywell measurements, helps to identify areas where potential sources of recharge from water-line leaks may exist.

Note: **All** wells are preceded by 299-

Laboratory Analyses. Extensive analyses were performed by the RCRA Corrective Action Program on the samples gathered from the boreholes. Because the amount of soil collected during the shallow vadose zone soil investigations was limited, analyses of those samples were much more selective. In addition to the RCRA Corrective Action Program activities, the national laboratories and universities investigated certain samples with highly advanced techniques.

Typical RCRA Corrective Action Program laboratory analyses included the measurement of physical properties (density, moisture content, specific conductivity) and elemental and isotopic concentrations. Concentrations were measured using water and strong acid extracts from the soil samples **as well as** using porewater. Anions typically investigated included nitrate, nitrite, chloride, fluoride, and sulfate. Cations typically investigated included aluminum, arsenic, boron, calcium, chromium, cobalt, iron, magnesium, manganese, molybdenum, nickel, potassium, selenium, silicon, sodium, strontium, and zinc. The major isotopes are technetium-99 and cesium-137. Isolated occurrences of slightly elevated uranium are present and very small quantities of iodine-129 are observed in the some soils from the SX-108 slant borehole.

Key findings from the RCRA Corrective Action Program-sponsored work include the following.

- Groundwater samples collected from groundwater wells 299-W23-15, 299-W23-19, 299-W22-48, 299-W22-49, 299-W22-50, 299-W22-80, 299-W22-81, and 299-W22-82 ranged from less than 10 pCi/L to 81,500 pCi/L for technetium-99. The drinking water standard is 900 pCi/L for technetium-99. The highest technetium-99 groundwater concentration on the Hanford Site is in well 299-W23-19. Multiple groundwater sources of technetium-99 within the WMA boundary are indicated.
- Analyses of tank farm soils show elevated concentrations of several constituents that are attributed to tank fluid leakage (primarily tanks SX-108 and SX-115) into the soil column. High concentrations of cesium-137 were found 16 to 30 m (52 to 100 ft) below ground surface, with concentrations **as high as** 96,000,000 pCi/g. High concentrations of more mobile contaminants (technetium-99, chromium, nitrate) in porewater or water extract samples were found deeper (down to 49 m [160 ft] below ground surface) in all 3 boreholes drilled inside the SX tank farm, primarily in the lower subunits of the Hanford formation (H1 and H2) and the upper Plio-Pleistocene unit (subunit PPlz). In the high-concentration depth intervals (21 to 49 m [70 to 160 ft] below ground), porewater concentrations **of** technetium-99 ranged from 95,000 to 240,000,000 pCi/L; chromium ranged from 3 to 21,800 mg/L; and nitrate **from** 6,000 to 1,000,000 mg/L.
- The bulk of the matric potential measurements for sediments from four boreholes (W22-48, W22-50, W23-19, and W23-234) in and around WMA S-SX suggest a draining profile throughout the Hanford formation. For the two boreholes inside the tank farm the matric potential profiles indicate draining throughout the vadose zone. For two boreholes outside the tank farm fences the matric potential profiles suggest that the anthropomorphic activities (removal of vegetation) resulted in an enhanced wetting front that has traveled through the Hanford formation and is presently very slowly wetting the deeper sediments. That is, for the two boreholes outside the tank farm fences, the deeper

sediments in the Plio-Pleistocene unit and Ringold Formation are wetting as opposed to draining.

The Science and Technology activity of the Hanford Groundwater Vadose Zone Integration Project conducted focused fundamental research in the areas of mineralogy, geochemistry, reactive transport modeling, and determination of field hydrologic parameters to address specific tank farm vadose zone issues. Laboratory experiments on tank farm sediment have provided results that led to an understanding of complex relationships between sodium ion concentrations and the mobility of cesium-137 in the Hanford vadose zone. Other laboratory studies have led to the development of a plausible hypothesis to explain the unexpected 'apparent' retardation of chromium(VI) in the Hanford sediments. These studies indicate that approximately 50% of the chromium(VI) may be immobilized in the vadose zone by post emplacement reduction to chromium(III). Desorption kinetic studies with chromium and cesium contaminated sediments have produced release-rate models that can be used for defensible projections of the future mobility of these sorbed contaminants. Isotope geochemistry studies have suggested that additional insight into multiple tank leak events can be developed by coupling Hanford irradiated fuel composition records with trace isotope analyses. Fluid flow, heat transport, and nonisothermal multiphase fluid flow and transport numerical modeling studies have provided considerable insight into the impacts of high-heat tank waste storage and leakage on the vadose zone geochemical environment. Finally, large-scale field investigations provide a better understanding of realistic hydrologic parameters required for transport modeling studies.

In particular, a key finding from this Science and Technology activity effort is that:

- The mobility of cesium is now quantitatively understood.

Cesium is quite mobile under high aqueous sodium conditions (e.g., the initial phase of the tank SX-108 leak), but is highly retarded for low concentrations of sodium (e.g., SX-115 leak). Thus, the observations that greatly contributed to the creation of the RCRA Corrective Action Program (the unexplained presence of a material far from its source, which was thought to be highly retarded in its movement) are now explained. Central to this explanation is the current belief that sodium concentrations in some of the leaked tank supernate (e.g., SX-108) were higher than originally thought. These concentrations may have exceeded 15 mol/L, a concentration that virtually eliminates the retardation of cesium. The existence of these high sodium concentrations, which resulted from the boiling and self-concentration of the wastes, was suggested by modeling performed by the Science and Technology effort and porewater characterization data from the slant borehole samples.

Data Evaluation. Data from previous efforts and from current laboratory measurements were extended by data evaluation efforts, particularly in the areas of inventory, recharge, and thermal modeling.

Previous estimates of soil inventories resulting from the major tank leaks have been enhanced. Improved estimates of in-tank inventories as a function of time have been derived from the Hanford defined waste model, thus allowing better estimates of the composition of the waste at the time of leak. Because of the extensive measurements of cesium-137 soil concentrations and because of the known ratios of other contaminants to cesium-137 in tank waste, cesium-137

became a key contaminant for inventory analyses. Multiple kriging analyses were completed using a variety of cesium-137 data sources. In particular, the last analysis included gamma data from existing boreholes, lateral tubes beneath the tanks, as well as cesium-137 concentrations from soil samples gathered in this field investigation. Combining the results of these efforts with contaminant concentrations from the new borehole samples greatly increased the knowledge of the level and extent of the leaked waste.

Key inventory estimates for WMA S-SX include the following:

- The total amount of tank waste leaked is 435,275 L (115,000 gal), with 90,800; 57,500; 56,775; and 189,250 L (24,000; 15,200; 15,000; and 50,000 gal) leaked, respectively, from tanks S-104, SX-108, SX-113, and SX-115.
- The total amount of cesium-137 leaked in the SX tank farm is 100,000 Ci, with 41,000 Ci from tank SX-108 as well as 19,000 Ci from tank SX-115 and 17,000 from tank SX-107.
- The total amount of technetium-99 leaked in the SX tank farm is 30 Ci, with 12 Ci from tank SX-108 as well as 5.5 Ci from tank SX-115 and 5 Ci from tank SX-107.

Because no site-specific recharge measurements are available, estimates of natural recharge are based primarily on analogous Hanford Site measurements (e.g., lysimetry studies). Results of an evaluation of recharge conducted to estimate drainage through the vadose zone indicate that natural and artificial recharge influence contaminant migration. Shedding from the tank domes enhances recharge. In the absence of site-specific data, natural recharge estimates at the tank farm are assumed to range from 10 mm/yr (0.4 in./yr) to 100 mm/yr (4.0 in./yr). Artificial recharge due to leaking water lines can overwhelm natural recharge and hence significantly enhance contaminant migration, as suggested by the groundwater measurements near tank SX-115.

The Science and Technology activity of the Hanford Groundwater Vadose Zone Integration Project performed a series of numerical simulations to investigate the effects of temperature on moisture flow. The temperatures in many SX tanks exceeded 100 °C (212 °F) in the 1950s and 1960s because of the high concentration of short-lived fission products in the REDOX high-level waste. The simulations indicate that there was significant dry-out of the soils beneath such tanks, and that the presence of a 'heat pipe' effect may have caused liquid moisture to move from surrounding vadose zone sediments toward the tank. A key finding is that:

- Thermal effects will have minor impact on moisture movement (and hence contaminant transport) after year 2000. However, in-ground temperatures are and will remain well above ambient temperature at depth in the vadose zone, and such temperatures do have implications for both chemical and hydrologic processes.

Section 3.5, Interim Measures

The field investigations for WMA S-SX suggest that anthropomorphic water sources have resulted in accelerated contaminant migration. Therefore, interim measures were identified and have been completed to minimize the infiltration from these sources. These interim measures include the following:

- Upgradient surface water run-on control measures
- Cut and capped two water lines running to the SX tank farm and leak-tested two water lines running to the S and SY tank farms
- Released water-line status maps for the S, SX, and SY tank farms.

The Office of River Protection has implemented interim measures related to upgradient surface water run-on control measures, cutting and capping water lines at other 200 West Area tank farms and plans to implement these same interim measures in the 200 East Area during fiscal year 2002. The key finding is that:

- The leak testing and cutting of water pipelines and building of run-on/run-off barriers should be performed for all single-shell tank farms.

Efforts have also been started to investigate the feasibility of remediating the groundwater technetium in the vicinity of the tank SX-115 borehole (well 299-W23-19).

Section 4.0, Summary and Conclusions of the Impact (Risk) Evaluations

To estimate the future impact of past tank leaks, a suite of numerical simulations was performed. For the most important simulations, the results were converted into risk values.

*Modeling Data Package for S-SX Field Investigation Report (FIR)*⁹ provided the models and parameters used in the two-dimensional numerical simulations for the 13 cases studied. The simulations started in the year 2000, using an initial contaminant distribution in the vadose zone based on the results of the inventory data evaluation. A period of 1,000 years was simulated. Potential leaks from tank waste retrieval and from tank closure were not included. In all scenarios, a final closure barrier was in place by 2040. Important cases analyzed the effect of an interim surface barrier, different recharge rates, and the initial distribution of contaminants in the vadose zone. The modeling focused primarily on the WMA S-SX boundary. To meet the requirements established by the Washington State Department of Ecology, three additional compliance points were analyzed at the 200 West Area fence, 200 Area exclusion zone boundary, and the Columbia River.

Key findings from the numerical simulations include the following.

- Projected groundwater concentrations for technetium-99, nitrate, and chromium exceeded the drinking water standard³ at the WMA S-SX boundary for all scenarios and cases except for projected nitrate groundwater concentrations for the two low recharge cases (i.e., 30 and 10 mm/yr).

⁹ Khaleel, R., T.E. Jones, A.J. Knepp, F.M. Mann, D.A. Myers, P.M. Rogers, R.J. Serne, and M.I. Wood, *Modeling Data Package for S-SX Field Investigation Report (FIR)*, RPP-6296, Rev. 0, CH2M Hill Hanford Group, Inc., Richland, Washington.

- For the base case (100 mm/yr recharge and a closure surface barrier) and the case having an interim surface barrier, simulated technetium concentrations exceed the drinking water standard at the WMA S-SX boundary and 200 West fence.
- For the base case, the estimated arrival times of the peak concentration for technetium-99 at the WMA S-SX boundary is estimated to be year 2046.
- The placement of an interim surface barrier in the year 2010 would reduce peak technetium-99 concentrations at the WMA S-SX boundary by about a factor of 2, yielding peak concentrations still above drinking water standards.
- The key factors affecting the estimation of risk near the S and SX tank farms as estimates of vadose zone contaminant inventory and recharge.

Arrival times for peak concentrations for chromium and nitrate are projected to be similar to those for technetium-99, with the differences being primarily due to the initial inventory distributions. Because of its retardation factor and radioactive decay, cesium-137 is projected to be undetectable at the WMA S-SX boundary for all simulation runs.

The interim surface barriers, as expected, reduce fluxes to the water table. The technetium-99 peak concentrations were reduced by over a factor of 2 with placement of barriers that causes the earlier reduction of recharge relative to the base case (which has only a closure surface barrier). However, the use of interim surface barriers did not result in projected contaminant concentration levels below drinking water standard maximum contaminant levels.

Simulation results indicate that two key drivers affecting future contaminant migration are estimates of vadose zone contaminant inventory and recharge. The contaminant inventories have a major influence on the peak concentrations and arrival times of long-lived mobile radionuclides and chemical species at the WMA S-SX boundary. The inventory mass (i.e., curies or kilograms) has a much more significant influence on estimated groundwater concentrations than the spatial distribution of the contaminants. Sensitivity analyses indicate that recharge estimates have a major influence on the peak concentrations and their arrival times. As discussed earlier, no tank farm-specific recharge estimates are presently available.

Risk and dose were evaluated for five of these 13 cases using the *Hanford Site Risk Assessment Methodology*¹⁰ and “Model Toxics Control Act”¹¹ Method B (unrestricted) and Method C (industrial) exposure scenarios. The major findings include the following.

- Incremental lifetime cancer risk ranges from 9.98×10^{-3} to 1.33×10^{-6} at the four points of compliance for the industrial worker scenario. Technetium-99 is the key contaminant of concern for cancer risk.

¹⁰ DOE-RL, 1995, *Hanford Site Risk Assessment Methodology*, DOE/RL-91-45, Rev. 3, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

¹¹ “Model Toxics Control Act,” RCW 70.105D, *Revised Code of Washington*, as amended.

- The hazard index ranges from 0.0045 to 300 at the four points of compliance for the industrial worker scenario. Chromium is the key contaminant of concern for the hazard index.

Section 5.0, Conclusions

Eight major outcomes have resulted from this work.

- A workable, effective approach has been developed to improve the characterization of vadose zone contamination in all the tank farm WMAs, to interpret past Contamination events, and to estimate future contaminant migration.
- A set of data collection activities has been completed to fill major gaps in the database that quantify the nature, extent, and mobility of contamination in the vadose zone. From these data, a conceptualization of contaminant migration events has evolved.
- Through cooperation with the Science and Technology activity of the Hanford Groundwater Vadose Zone Integration Project and other Hanford Site projects, resources normally unavailable to the RCRA Corrective Action Program were put to use on soil and groundwater issues. These activities provided significant insight into their resolution.
- The insertion of DOE national laboratory and university laboratory expertise was directed at important issues and yielded significant results over a very short time period.
- Future migration patterns and associated risk from groundwater contamination have been projected for the next 1,000 years.
- A series of interim measures have been identified and implemented that immediately reduce the potential of accelerated contaminant migration.
- The approach used by the RCRA Corrective Action Program is successful and should be used for future efforts. The approach of the RCRA Corrective Action Program (gather existing data, identify gaps, collect new data based on gaps, analyze the consequence of the data obtained, and document all the efforts) worked extremely well.
- The current conceptual model should be the basis for further RCRA Corrective Action Program activities and modeling.

In addition, some more general conclusions can be reached. These conclusions involve the approach taken by the program itself and the conceptual models used.

Prior to the initiation of the WMA S-SX characterization effort, a conceptual model was developed from the existing data to explain contamination events that lead to the current state of contamination in the WMA S-SX vadose zone and nearby unconfined aquifer. This conceptual model pictured the contaminant transport having two stages (an early stage driven by the chemical constituents of the leak including enhanced moisture flow, followed by a second stage

where the natural systems of the vadose zone reasserted themselves). In general, this conceptual model has been strengthened by the new information gathered.

Section 6.0, Recommendations

This section provides recommendations for further investigations and decisions based on findings from the WMA S-SX vadose zone and groundwater characterization activities. Recommendations for further investigations and decisions are provided for the following:

- Interim measures
- Accelerated corrective measure studies
- Future tank farm operations
- Collection of additional data and information
- Lessons learned
- Restructuring of the RCRA Corrective Action Program.

Interim Measures. Interim measures (leak testing and capping of waterlines as well as run-odrunk-off controls) were identified and have already been completed at WMAs S-SX, U, T, and TX-TY. Such measures should be performed for all tank farms and are planned.

Work has begun to test the feasibility of remediating the technetium groundwater plume identified at well 299-W23-19 located near tank SX-115. This work should continue to determine the need for and most appropriate means for remediation, if necessary.

Accelerated Corrective Measure Studies. A possible corrective measure would be the placement of interim surface barriers. Numerical simulation results suggest that compared to the final-surface-barrier-only alternative, placement of an interim surface barrier provides a twofold improvement in peak concentrations for mobile contaminants because of the earlier reductions in recharge. However, contaminant concentrations even with an interim barrier are still projected to be higher than drinking water standards. An engineering study with full tank farm staff involvement should be performed to determine the impacts from placing interim barriers inside the tank farms on tank farm operations as well as on waste retrieval and closure activities.

Future Tank Farms Operations. Numerous tank waste leaks have occurred in the SST farms through overfilling of tanks or through leaks in ancillary equipment (e.g., piping) during transfers of waste from one tank to another. This characterization program has shown how important the effects of manmade leaks from tank infrastructure have been in the migration history of tank leaks. Therefore, the recent use of aboveground piping and similar types of best management practices should be continued before, during, and after waste retrieval activities to minimize potential releases to the environment in the future during waste retrieval activities.

The new enhanced understanding of cesium migration implies that new sodium sources should not be applied to the vadose zone. Without such sources, the cesium-137 is not expected to move significant distances. Thus, future liquid waste retrieval activities should evaluate the use of either limited water-based or dry waste retrieval methods instead of sodium-rich Supernate as the waste retrieval media to ensure cesium does not migrate further downward, especially on known past leaking tanks like tank SX-108.

Collection of Additional WMA S-SX Data and Information. Additional data collection is warranted only if the data collected are anticipated to have a significant impact on the findings presented in this report. Additional data do not appear to be necessary to support interim action decisions.

To reduce uncertainty, additional data could be obtained in WMA S-SX:

- Quantify gamma activity directly beneath the tanks through the use of the laterals located beneath SX farm tanks
- Quantify recharge rates for tank farm sediments
- Obtain vadose zone samples near tanks SX-107, S-104, and SX-115 and analyze those samples for important contaminants.

The matric potential and moisture measurements for sediment samples in WMA S-SX are valuable in determining the tank farm soil moisture regime and potential for contaminant migration. These measurements can and should be extended to other tank farms. In FY 2001, a plan similar to that used for analyses of gross gamma measurements was developed to analyze previously collected moisture content measurements. Such analyses should be performed for all SST farms to aid in identifying opportunities for enhanced contaminant migration.

Data and models have been developed by the Science and Technology activity that can be used to evaluate the effects of aqueous sodium releases on the remobilization of cesium-137 that is sorbed to sediments in the vadose zone. These models can be used to evaluate the effects of different retrieval scenarios and leak losses on the stability of the sorbed, in-ground cesium pool.

Lessons Learned. Much has been learned from the characterization, laboratory analyses, and modeling done for WMA S-SX. For example, the drilling techniques developed from the SX-108 slant borehole may be applied to characterization of the TX tank farm. The use of a tiered analysis approach has greatly decreased costs while prioritizing areas of greatest interests. Finally, non-isothermal and isothermal modeling has improved the assessment of future releases to the groundwater and an understanding of thermal effects for contaminant migration through the vadose zone.

The main lesson learned is the approach used in creating this field investigation report was successful and should be repeated for other field investigation report efforts. The FIRs will provide the baseline information to support tank waste retrieval and tank farm closure.

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LIST OF TERMS

bgs	below ground surface
BTC	breakthrough curve
CHG	CH2M HILL Hanford Group, Inc.
CMS	corrective measures study
CoC	contaminant of concern
CoPC	constituent of potential
DOE	U.S. Department of Energy
DQO	data quality objectives
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
FIR	field investigation report
FY	fiscal year
HDW	Hanford defined waste (model)
HFFACO	<i>Hanford Federal Facility Agreement and Consent Order</i>
HGL	HydroGeologic, Inc.
HLW	high-level waste
HSRAM	Hanford Site Risk Assessment Methodology
ICM	interim corrective measure
ILCR	incremental lifetime cancer risk
MSU	Montana State University
MTCA	Model Toxics Control Act
ORP	Office of River Protection
RCRA	<i>Resource Conservation and Recovery Act of 1976</i>
REDOX	reduction-oxidation
RFI	RCRA facility investigation
RPP	River Protection Project
S&T	Science and Technology
SST	single-shell tank
TWRS EIS	Tank Waste Remediation System Environmental Impact Statement
WMA	waste management area

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1.0 INTRODUCTION

This *Field Investigation Report for Waste Management Area S-SX* has been prepared for the *Resource Conservation and Recovery Act of 1976 (RCRA) Corrective Action Program* for single-shell tank (SST) farms at the U.S. Department of Energy (DOE) Hanford Site. The DOE Office of River Protection (OW) initiated the SST RCRA Corrective Action Program to address the nature and extent of contamination and associated risk impacts of past and potential future tank waste releases to the environment. This document is prescribed under the *Hanford Federal Facility Agreement and Consent Order (HFFACO; Ecology et al. 1989)* that is signed by the Washington State Department of Ecology (Ecology), the U.S. Environmental Protection Agency (EPA), and DOE. Issuance of this document to Ecology fulfills HFFACO Milestone M-45-55-T01.

This document fulfills the SST RCRA Corrective Action Program process criteria between completion of the initial site-specific field investigations at waste management area (WMA) S-SX and preparation of an RCRA facility investigation (RFI) report for the eight SST farms (i.e., S, SX, B, BX, BY, T, TX, and TY) that are currently part of the SST RCRA Corrective Action Program. Figure 1.1 provides a logic diagram of the RCRA Corrective Action Program process.

**Figure 1.1. Resource Conservation and Recovery Act
Corrective Action Process Flow Diagram**

Placement of the WMA S-SX field investigation report (FIR) at this point in the process facilitates an early opportunity for decision makers to consider implementation of interim measures or an accelerated interim corrective measures study (CMS) at WMA S-SX. This document closely parallels the structure of an RFI report because the intent of the Tri-Parties

(i.e., Ecology, EPA, and DOE) is to combine this document with two other FIRs that will then become the basis of one consolidated RFI report that addresses the eight SST farms.

1.1 PURPOSE AND OBJECTIVES

Based on a high-level annotated outline defined in Appendix H of *Phase I RCRA Facility Investigation/Corrective Measures Study Work Plan for Single-Shell Tank Waste Management Areas* (DOE-RL 2000), a FIR has two major documentation functions that define the overall approach.

- Document the data. This includes the sampling approaches, the data itself, initial data reduction, and interpretation of subsurface conditions. The sampling approaches and resulting data are associated with site-specific WMA field characterization efforts. Data from other sources are integrated into the site-specific WMA data to enhance the interpretation of subsurface conditions. The data include geologic, hydrologic, geochemical, and vadose zone contaminant inventories.
- Document the impact assessment of various conditions and scenarios. This includes an assessment of present conditions and early identification of those areas that may require an interim measure or accelerated interim corrective measure (ICM) that might be applied to the WMA. These assessments provide predictions of groundwater impacts and associated human health risks at compliance point(s) over a period of 1,000 years.

The purpose of this WMA S-SX FIR is to fulfill the following:

- Summarize data and evaluations from the site-specific field investigation activities at WMA S-SX and from other information sources
- Evaluate the data to the extent necessary to determine the potential risk associated with hypothetical exposure to soil and groundwater at the WMA boundary
- Recommend one or more interim measures to mitigate the risk or initiation of an accelerated CMS to evaluate and compare more complex ICMs, if the potential for near-term risk is excessive
- Collect data to support waste retrieval from SSTs

The project objectives fulfilled in this document are defined in the two work plan addenda for this effort: *Preliminary Site-Specific SST Phase I RFI/CMS Work Plan Addendum for WMA S-SX* (Henderson 1999) and *Site-Specific SST Phase I RFI/CMS Work Plan Addendum for WMA S-SX* (Rogers and Knepp 2000) and *Activity Plan: Extension of Borehole 41-09-39 SX Tank Farm* (Myers 1997). The objectives identified in the work plan addenda are as follows:

- Collect data to support an improved understanding of the nature and extent of contaminants in the vadose zone from surface to groundwater
- Collect data to support an improved understanding of the nature and extent and fate and transport of contaminants to perform a risk assessment

- Provide WMA-specific information on source, nature, and extent of contamination for planned activities identified in the work plans
- Provide WMA-specific characterization programs data to address data gaps identified through a data quality objectives (DQO) process.

In accordance with the Phase 1 RFI/CMS work plan (DOE-RL 2000), this document includes a qualitative and limited assessment of contamination impacts on human health, but it does not include evaluations of impact to ecological receptors.

1.2 OVERVIEW

The Hanford Site is managed by DOE and encompasses approximately 1,517 km² (586 mi²) in the Columbia Basin of southcentral Washington State. The Hanford Site is divided into a number of waste management units, including the 200 Areas located near the center of the Site. The 200 Areas comprise the 200 East, 200 West, and 200 North Areas. The 200 East and 200 West Areas contain waste management facilities and inactive, irradiated fuel-reprocessing facilities. The 200 North Area was formally used for interim storage and staging of irradiated fuel. Some of these waste management sites are treatment, storage, and/or disposal units that include the SSTs.

The 149 SSTs, which are grouped into 12 SST farms, are regulated under the Washington State “Hazardous Waste Management Act” and its implementing requirements in the state “Dangerous Waste Regulations” (WAC 173-303). Waste in these SSTs consists of liquid; sludges; and salt cake (i.e., crystallized salts). Over the years, much of the liquid stored in the SSTs has been evaporated or pumped to double-shell tanks. The SSTs are operating under interim status pending closure. The 12 SST farms are grouped into 7 WMAs for the purpose of groundwater monitoring. Closure of the SST farms is the largest project at the Hanford Site and involves numerous activities aimed at the design, construction, and operation of waste retrieval, treatment, and storage facilities. Cleanup of the SSTs is under the purview of the ORP and River Protection Project (RPP). CH2M HILL Hanford Group, Inc. (CHG) is the current tank farm contractor in charge of carrying out the RPP mission at the tank farms. All projects associated with vadose zone characterization at the tank farms are under purview of the CHG Tank Farm Vadose Zone Project. All groundwater monitoring at the tank farms is under the purview of Pacific Northwest National Laboratory and is integrated with the Tank Farm Vadose Zone Project through the Hanford Groundwater Vadose Zone Integration Project.

The S and SX tank farms comprise WMA S-SX. These tank farms are located in the southern portion of the 200 West Area, near the Reduction-Oxidation (REDOX) Plant (Figure 1.2).

The S tank farm is comprised of the following:

- 12 SSTs, each with a 2,900,000 L (758,000 gal) capacity
- Waste transfer lines
- Leak detection systems
- Tank ancillary equipment.

Figure 1.2. Location Map of Single-Shell Tank Waste Management Area S-SX and Surrounding Facilities in the 200 West Area

The SX tank farm is comprised of the following:

- 15 SSTs, each with a 3,785,000 L (1 million gal) capacity
- Waste transfer lines
- Leak detection systems
- Tank ancillary equipment.

The SSTs in both tank farms are 23 m (75 ft) in diameter. The S farm SSTs are approximately 11.4 m (37.3 ft) tall from base to dome, and the SX farm SSTs are approximately 13.4 m (44 ft) tall from base to dome. The sediment cover from the apex of a tank dome to ground surface is approximately 2.5 m (8.1 ft) at the S tank farm and 1.8 m (6 ft) at the SX tank farm. The general configuration of tanks in WMA S-SX is shown in Figure 1.3. The SX farm SSTs were the first SSTs designed for self-boiling (i.e., self-concentrating) waste; however, the S farm SSTs received REDOX Plant waste that self-boiled. The S and SX farm SSTs were constructed with cascade overflow lines in three-tank series to allow gravity flow of liquid waste between the tanks. These cascade lines were not used in the SX tank farm. Ten of the 15 tanks in the SX tank farm and 1 of the 12 tanks in the S tank farm are classified as assumed leakers (Hanlon 2001).

The following sections provide an overview of the background conditions at WMA S-SX and the role of this FIR in the overall regulatory framework.

1.2.1 General Background

WMA S-SX was placed in assessment groundwater monitoring in August 1996 because of elevated specific conductance and technetium-99 in downgradient monitoring wells (Caggiano 1996). Technetium-99, nitrate, uranium, gross alpha, gross beta, tritium, iron, manganese, carbon tetrachloride, and aluminum are the only constituents to have exceeded drinking water standards (Johnson and Chou 1998).

Spectral gamma logging (i.e., collection of baseline gamma-specific radioisotope information in the upper vadose zone) was completed at the SX tank farm in fiscal year (FY) 1995 and at the S tank farm in FY 1996. The spectral gamma logging program builds on a previous program in which gross gamma data were collected as a means of leak detection from the SSTs.

Both programs used the network of drywells installed around each tank in each SST farm.

Vadose Zone Characterization Project at the Hanford Tank Farms: SX Tank Farm Report (DOE-GJPO 1996), dated July 1996, is the report on spectral gamma logging at the SX tank farm and indicates contaminant cesium-137 at a maximum depth of 43 m (140 ft) below ground surface (bgs) near tank SX-102 and contaminants at depths of 39.6 m (130 ft) bgs near tanks SX-108 and SX-109. *Hanford Tank Farms Vadose Zone S Tank Farm Report* (DOE-GJPO 1998), dated February 1998, is the report on spectral gamma logging at the S tank farm and indicates contaminants cesium-137, cobalt-60, and europium-154 at a maximum of 18.3 m (60 ft) bgs near tank S-102 and cesium-137 at 29 m (95 ft) bgs near tank S-104.

The network of drywells installed around each tank was intended for leak detection and was generally installed between 22.8 m and 45.7 m (75 to 150 ft) bgs; thus, the maximum detection depth is limited by the drywell depth.

Figure 1.3. General Configuration of Tanks in Waste Management Area S-SX

In 1996 DOE formed a panel to evaluate issues associated with vadose zone contamination in the Hanford Site tank farms. Following a review of available data, the panel recommended a series of measures to improve characterization of the vadose zone and recommended installation of new boreholes in the SX tank farm to address issues associated with contaminant migration through preferential pathways (e.g., boreholes) and through the Hanford formation (DOE-RL 1997b; DOE-RL 1999d). Two new drywells were installed (boreholes 41-12-01 and 41-09-39).

Based on the information obtained from the extension of borehole 41-09-39 (Myers et al. 1998) and the results of the groundwater assessment for WMA S-SX (Johnson and Chou 1998), the two site-specific work plans (Henderson 1999; Rogers and Knepp 2000) were prepared. The work plans describe the following field investigation activities:

- Decommissioning (i.e., abandonment) and sediment sampling of the upper portion (0 to 39.6 m [0 to 130 ft] bgs) of borehole 41-09-39 (Henderson 1999)
- Installation of a new borehole southwest of tank SX-115 (well 299-W23-19) (Henderson 1999)
- Sampling of a new RCRA groundwater monitoring well south and southeast of the SX tank farm (well 299-W22-50) (Henderson 1999)
- Slant borehole northwest of tank SX-108 extending beneath the tank (Rogers and Knepp 2000)
- Near-surface characterization in the S tank farm (Rogers and Knepp 2000).

These five characterization activities provided the data to support the nature and extent of contamination collected from the field investigations conducted in WMA S-SX. These activities contribute to the basis for the conclusions and recommendations of this report.

Ongoing Hanford Site programs and projects that also contribute to the FIR evaluations include the following:

- Hanford Groundwater Vadose Zone Integration Project
- Integrated Technology and Research Demonstration Project
- Environmental restoration of past-practice sites
- Hanford Site Groundwater Monitoring Program.

These programs and projects all provide valuable data and information that are expected to enhance the FIR evaluations.

1.2.2 Regulatory Framework

Based on the results of the groundwater assessment, Ecology requested on July 10, 1998 that DOE develop and submit a corrective action plan for the four WMAs with documented leaks (i.e., WMAs S-SX, B-BX-BY, T, and TX-TY). Pursuant to HFFACO Change Package M-45-98-03 and the Phase 1 RFI/CMS work plan (DOE-RL 2000), the RCRA Corrective Action

Program process is used to establish the framework within which vadose zone investigations at the SSTs are planned and implemented. The sequence of investigations and evaluations for WMA S-SX, as prescribed in the Change Package, is as follows:

- Initiation of preliminary characterization efforts in FY 1999 based on the preliminary work plan addendum (Henderson 1999) to fulfill HFFACO Milestone M-45-52-TO1
- Characterization of the remainder of WMA S-SX in FY 2000 based on the work plan addendum (Rogers and Knepp 2000) to fulfill HFFACO Milestone M-45-52
- Preparation of this document, the *Field Investigation Report for Waste Management Area S-SX*, in FY 2001 and FY 2002 to fulfill HFFACO Milestone M-45-55-TO1
- Preparation of an RFI report in FY 2003 and FY 2004 that rolls up the results and recommendations from the FIRs on WMAs S-SX, B-BX-BY, T, and TX-TY to fulfill HFFACO Milestone M-45-55.

This sequence is illustrated in Figure 1.1.

1.3 DOCUMENT STRUCTURE

This report follows the prescribed outline for a FIR provided in Appendix H of the Phase 1 RFI/CMS work plan (DOE-RL 2000). Seven sections and nine appendices are included in this WMA S-SX FIR. The document is structured to provide the information necessary to describe the vadose zone and associated groundwater field and laboratory investigation results at WMA S-SX from 1997 to present. The following are the sections and appendices that comprise this report.

- **Section 1.0** – Introduction to the WMA S-SX FIR that provides an overview of background and purpose.
- **Section 2.0** – Overview of the investigative approach that is based on two work plans and an activity plan. Deviations from the plans are also addressed. Environmental setting and potential contamination information before the field investigation activities commenced under the RCRA Corrective Action Program are described.
- **Section 3.0** – Summary of the major findings of the field investigations and associated analyses and the interim measures and ICMs available for implementation.
- **Section 4.0** – Summary of the methodology and results for potential impacts to human health and the environment based on numerical modeling. The contaminant exposure pathways used in the numerical modeling conceptual exposure pathway model for WMA S-SX are presented. A comparison of these results to regulatory standards is provided.
- **Section 5.0** – Conclusions based on information provided in Sections 3.0 and 4.0.
- **Section 6.0** – Recommendations based on the conclusions.

- **Section 7.0** – List of the references used to develop the WMA S-SX FIR main text.
- **Appendix A** – Details of the investigative approach developed in the work plan addenda to support characterization efforts.
- **Appendix B** – Results of the work plan field investigation activities.
- **Appendix C** – Field and laboratory results developed through the integration process that were not directly collected in the field based on the work plans. This appendix presents interpretation results developed from geological, geophysical, hydrologic, and inventory data.
- **Appendix D** – Science and Technology (S&T) activities evaluation of data related to chemical and physical attributes of the effects of the waste stream related to WMA S-SX.
- **Appendix E** – Impact assessment approach and results derived from numerical modeling and the associated human health risk and dose.
- **Appendix F** – Cost and implementability of ICMs and interim measures at WMA S-SX.
- **Appendix G** – Regulatory analyses based on field investigation results.
- **Appendix H** – Quality assurance and quality control documentation for sampling and laboratory procedures in conjunction with RCRA regulations.
- **Appendix I** – List of the preparers of the WMA S-SX FIR.

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2.0 INVESTIGATIVE APPROACH

This section describes the investigative approach used in this WMA S-SX FIR. The regulatory framework for the investigative approach used in the WMA S-SX field investigation ~~was~~ developed through negotiations with Ecology and DOE in HFFACO Change Package M-45-98-03. The technical framework for the investigative approach that identifies data needs ³ provided in *A Summary and Evaluation of Hanford Site Tank Farm Subsurface Contamination* (Jones et al. 1998). The Phase 1 RFI/CMS work plan (DOE-RL 2000), preliminary work plan addendum (Henderson 1999), and work plan addendum (Rogers and Knepp 2000) provide the documentation for implementation of the field investigation activities. Appendix A provides detailed information on the investigative approach. The Phase 1 RFI/CMS work plan provides a single document that encompasses the aspects common to all WMAs and establishes the regulatory and programmatic framework for the overall RCRA Corrective Action Program. The other two documents are site-specific work plan addenda for WMA S-SX. Before initiation of the RCRA Corrective Action Program, a vadose zone investigation was conducted in the SX tank farm. Reference to *Activity Plan: Extension of Borehole 41-09-39, SX Tank Farm* (Myers 1997) is included in this report for completeness to acknowledge all recent vadose zone characterization activities conducted at WMA S-SX. The investigative approach was greatly enhanced by the carefully selected field investigations discussed in the work plans. The work plans provide a basis for verifying the extensive knowledge base that exists for WMA S-SX associated with geology; hydrology; geophysics; groundwater chemistry; waste chemistry; and releases from the tank systems (i.e., transfer pipelines). These selected field investigations provide a basis for integrating extensive databases that lead to a reasonable understanding of the important contaminants of concern (CoCs). These contaminants are modeled and the transport modeling results then lead to human health risk assessments to assist in determining whether implementation of interim measures are required.

To ensure appropriate data are collected to meet the needs for the FIRs as identified in site-specific work plans, an implementation plan is prepared as Appendix J of the Phase 1 RFI/CMS work plan (DOE-RL 2000). Key to the implementation plan approach is first understanding what evaluations would be most appropriate for a FIR and then addressing assimilation of data necessary to complete those evaluations. As documented in Appendix J of the implementation plan, the key evaluation for assessing effectiveness of interim measures and the need for additional data would be that of the potential risk to a human receptor.

The needs to complete the WMA S-SX evaluation are complicated and the answers to those needs become less certain when WMA-specific factors are considered. Those factors include the following:

- Long time span over which the SSTs operated (i.e., 1950 through 1980)
- High cost of site-specific data collection
- Transient geochemical conditions that have existed from the time of waste releases to present

- Associated cribs and waste sites adjacent to the WMA boundary that have contributed to groundwater contamination with the same CoCs.

2.1 PREVIOUS DATA AND INFORMATION

Because so much data on the S and SX tank farms exist, the site-specific work plan addenda (Henderson 1999; Rogers and Knepp 2000) include the following actions:

- Collect and assimilate previously obtained data including that related to tank inventory; planned and unplanned releases; subsurface conditions; and occurrences (e.g., leaking water lines)
- Develop a preliminary understanding of the distributions of contaminants in the vadose zone from review and evaluation of the gross gamma and spectral gamma geophysical logs
- Identify additional data needs
- Identify methods to gather data to address the data needs through a DQO process.

2.1.1 Previously Obtained Data

Because of the large amounts of existing S and SX tank farms data, only a summary of that collected and assimilated data is given in this report. The Tank Farm Vadose Zone Project created *Subsurface Physical Conditions Description for S-SX Waste Management Area* (Johnson et al. 1999) to be the primary reference for such previous knowledge. However, for the preliminary work plan (Henderson 1999), data obtained prior to Johnson et al. (1999) provided the planning basis for the RCRA site-specific investigations and the framework for the initial generalized conceptual models. The following are the major supporting data documents for Henderson (1999):

- *Historical Tank Content Estimate for the Southwest Quadrant of the Hanford 200 West Area* (Brevick et al. 1994)
- *A Summary and Evaluation of Hanford Site Tank Farm Subsurface Contamination* (Jones et al. 1998)
- *Vadose Zone Characterization Project at the Hanford Tank Farms, SX Tank Farm Report* (DOE-GJPO 1996)
- *Characterization of Subsurface Contamination in the SX Tank Farm* (Raymond and Shdo 1966)
- *Tank 241-SX-108 Leak Assessment* (WHC 1992a)
- *Tank 241-SX-109 Leak Assessment* (WHC 1992b)
- *Tank 241-SX-115 Leak Assessment* (WHC 1992c).

In these preparatory documents, existing data relevant to the tank waste leak events and associated vadose zone and unconfined aquifer contamination in WMA S-SX are summarized and used to develop conceptual models of the leak events and subsequent contaminant migration in the subsurface. Geologic descriptions of soils taken from boreholes, geophysical data, and water elevation measurements have been collected to quantify site-specific geologic and unconfined aquifer hydrologic characteristics. Historical records, gamma logging data, chemical and radiological sample analyses of site-specific soils and nearby groundwater, and sorptioddesorption data have also been collected to quantify soil column contamination. The most informative data from each of these topical areas are summarized in the following sections. Additional details are provided in Appendices B and C.

2.1.1.1 Hydrogeologic Data. A physical model of the geologic strata underlying WMA S-SX in the vadose zone and the unconfined aquifer was developed from numerous geologic well logs and geophysical logging data (e.g., gamma logging of naturally occurring radionuclides and moisture content from neutron logs) taken at boreholes and drywells within and near WMA S-SX. From these data, the characteristics (e.g., spatial orientation, thickness, particle size distribution) of the geologic units underlying WMA S-SX were developed. Consistency of the site-specific physical model with sitewide geology was also demonstrated.

The vadose zone and unconfined aquifer underlying WMA S-SX is made up of the three primary formations that are present throughout much of the Hanford Site:

- Ringold Formation, which rests on the underlying Columbia River Basalt Group
- Plio-Pleistocene unit, which overlies the Ringold Formation
- Hanford formation, which overlies the Plio-Pleistocene unit.

The thickness of the vadose zone for the Ringold Formation ranges from 15.8 m (52 ft) to 23.5 m (77 ft) from west to east. The thickness of the Plio-Pleistocene unit ranges from 11.6 m (38 ft) to 4.3 m (14 ft) from west to east. The thickness of the Hanford formation ranges from 37.2 m (122 ft) to 41.2 m (135 ft) from west to east. The thicknesses of these formations are based on wells 299-W23-19 and 299-W22-48. Based on previous data the thickness corresponds within 1.5 m (5 ft) of well 299-W23-19.

Directly underneath WMA S-SX, these strata tend to be of fairly uniform thickness and nearly flat-lying. Some units (i.e., Hanford formation subunit H1 and the Plio-Pleistocene unit) dip gently to the southwest. A more detailed description is provided in Section C.4.0 of Appendix C.

A subunit of particular interest is a gravel-rich layer in the Hanford formation, subunit H1, that lies close to the bottoms of tanks SX-107, SX-108, and SX-109 and that contains the majority of cesium-137 from leaks from these tanks. This association suggests that subunit H1 acted as a stratigraphic control for initial tank leak migration into the soil column.

At WMA S-SX the water table lies within the Ringold Formation. In 1998 the water table depth was about 65.5 m (215 ft) bgs and dropping. Both water level and general direction of groundwater flow in this region have been altered multiple times by high-volume wastewater discharges to various ponds throughout Hanford operations history. Most recently (i.e., 1980s) a groundwater mound in this area was maintained by liquid discharge to U pond just northwest

of WMA S-SX, elevating the water table and imposing a northwest to southeast trend in groundwater flow under WMA S-SX. Since the cessation of liquid discharge to U pond in 1985, the water table has been dropping about 0.6 m (2 ft) a year, and the general flow direction is rotating into a more easterly path. A water table depth of about 71.6 to 73.2 m (235 to 240 ft) bgs is anticipated when the groundwater mound completely dissipates.

2.1.1.2 Soil Contamination Data. The genesis and current state of contamination in the vadose zone and the unconfined aquifer underlying WMA S-SX is derived from three primary sources: the historical record, gamma logging data, and radiochemical and chemical analyses of soils and groundwater. The historical record identifies the following:

- Tank farm operations that supported various fuel processing, thereby providing the basis for estimating tank contents
- Specific tank leak events where liquid level measurements in the tanks or gamma radiation spikes measured in drywells surrounding the tanks indicate leakage of tank waste into the soil column
- Unplanned release events that discharged various amounts of fluids into the soil column.

Significant events provided in the record of S and SX tank farm history that relate to vadose zone contamination include several large leaks that occurred and contained substantial concentrations of contaminants (i.e., leaks from tanks S-104, SX-108, and SX-115). Leaks from other tanks are also assumed but their contributions to environmental contamination appear to be much less. The source of the waste that leaked from the tanks is primarily from the REDOX Plant (Section 3.0 and Jones et al. 2000a). Numerous unplanned releases are also known.

Two types of gamma ray logging data have been collected for WMA S-SX from a set of drywells placed around and between tanks in the S and SX farms. A gross gamma logging program operated from 1961 to 1994 (readily useable data are available dating from 1974) and a spectral gamma database was developed in the mid 1990s. Gross gamma logging of laterals extending under and across 7 tanks about 3.3 m (10 ft) below tank bottoms in the SX tank farm was also conducted. The gross gamma logging program provided a record of gross gamma intensities over time in numerous locations, allowing some perspective on the locations of contaminant occurrence and movement in the vadose zone over time and the fraction of total gamma-emitting contaminants involved in migration. The spectral gamma database provided a three-dimensional quantification of specific gamma-emitting radionuclide concentrations.

Soil sample analyses provide the most direct means of quantifying specific contaminants and their concentrations in the vadose zone. Analysis of gamma-emitting radionuclides (usually cesium-137) permits corroboration of gamma logging data. Two separate soil-sampling programs were completed prior to compilation of Johnson et al. (1999). In 1965 soils were sampled near tanks SX-108 and SX-115 at tank bottom depths; the cesium-137 concentration in those soils was determined from those samples (Raymond and Shdo 1966). Total waste volume and cesium-137 inventory lost was estimated from the soil sample data, gross gamma data from nearby drywells and laterals, and supernate analyses.

In 1998 samples were taken from borehole 41-09-39, located southeast of tank SX-108, and analyzed (Myers et al. 1998). For this study the borehole was extended from about 39.6 m (130 ft) bgs to groundwater, about 65.5 m (215 ft) bgs. Contamination in this borehole comes primarily from the tank SX-108 leak. Geophysical logging was completed. Samples between 39.9 and 65.2 m (131 and 214 ft) bgs were analyzed for radionuclides and inorganic chemistry. Soils were also leached with water, which was subsequently analyzed for radionuclides, inorganic constituents, pH, and electrical conductivity. These analyses showed that relative concentrations of cesium-137, technetium-99, and nitrate originating in the tank waste change as a function of depth, providing an indication of tank waste migration in the vadose zone over the last 40 years. Cesium-137 concentrations peak at around 40 and 41 m (131 to 135 ft) bgs and technetium-99 concentrations peak around 41 m (135 ft) bgs.

Sorption and desorption experiments conducted on some of the collected soil samples with a variety of liquids, including both tank and groundwater simulants, showed that cesium-137 sorption, normally quite high under disturbed conditions, can be substantially reduced by introducing large concentrations of sodium into the environment. Desorption experiments showed that cesium-137 is currently highly immobile in these soils as long as natural water contacts these soils.

Recent groundwater contaminant data in RCRA monitoring wells surrounding tank farms provide indications of tank waste having reached the unconfined aquifer (Johnson and Chou 1998; Johnson and Chou 1999). Significant data include elevated concentrations of constituents in groundwater also known to be present in the vadose zone because of tank leaks and knowledge of groundwater flow direction derived from water table levels in the monitoring network. When these data are combined with the identification of potential upgradient sources in the vadose zone, general causal relationships can be inferred. Wells surrounding WMA S-SX have shown transient elevated levels (spikes) of technetium-99, nitrate, and chromium in wells running along the southern edge of the SX tank farm and along the eastern edges of the S and SX tank farms since 1986.

When considering all the data provided by the four main sources of information, the primary observation is that three main areas of contamination exist in the vadose zone underlying WMA S-SX. These include the areas around the following:

- Tanks SX-107, SX-108, SX-109
- Tank SX-115
- Tanks-104.

There is fairly strong evidence from the historical record that the largest leaks in WMA S-SX came from these tanks or associated infrastructure and that the primary gamma-emitting radionuclide still in the vadose zone is cesium-137. Comparison of gamma data **within** these three areas shows cesium-137 to be much more extensively distributed both horizontally and vertically in the area around tanks SX-107, SX-108, and SX-109. In the areas around tanks SX-115 and S-104, cesium-137 is measured in one drywell very close to the side of each tank.

2.1.2 Conceptual Models

Conceptual models provided in Johnson et al. (1999) and Jones et al. (1998) integrate available data into plausible hypotheses of events and controlling physical and chemical processes that have caused the current state of contamination in the vadose zone and unconfined aquifer. Hypotheses have been developed for each of the three main areas of contamination because the database suggests enough differences in contaminant occurrence and migration exist in the different areas to warrant distinct explanations. The conceptual models were developed to aid the evaluation of potential impacts and to plan additional characterization efforts.

In Johnson et al. (1999), the contamination in the area around tanks SX-107, SX-108, and SX-109 is described as being focused on a leak from tank SX-108. Outstanding features of this contamination event included the following:

- High cesium-137, sodium, and aluminum concentrations in the supernate
- Apparent rapid and high-volume discharge
- Extensive horizontal and vertical extent of cesium-137 Contamination in the vadose zone
- Slightly contaminated groundwater directly below these three tanks.

From these observations, a gross two-step process for how the leak occurred was postulated. In the first step, rapid release of the leaking fluid occurred, forcing fluid to move rather rapidly through the vadose zone. Stratigraphic variability in the vadose zone geology exerted sufficient influence to induce a high degree of movement in the horizontal direction to the southwest. The supernate chemistry controlled the local geochemical conditions to greatly mobilize cesium-137 (sodium successfully competing with cesium-137 for sorption sites) so that it was poorly retarded and migrated essentially with the tank fluid. In the second step, the hydraulic impetus of the leak event ceased and water movement reverted to control of natural infiltration that induced slow downward percolation. Local water chemistry conditions reverted to more natural soil-water conditions causing cesium-137 to sorb strongly. Subsequent movement of cesium-137 has been minimal. Technetium-99 and other mobile constituents, nitrate and chromium, remain mobile but are migrating rather slowly. Minimal groundwater contamination in the immediate vicinity suggests that little if any contamination from these sources **has** reached the unconfined aquifer.

Outstanding features of contamination in the area around tank SX-115 include the following:

- Dilute fluid chemistry relative to tank SX-108 supernate, including cesium-137 concentrations one tenth of that in tank SX-108 supernate
- Apparent rapid and high-volume discharge from the tank bottom into the soil column
- High cesium-137 concentrations in the soil column measured near one edge and beneath tank SX-115
- Inferred large water-line leakage west and south of tank SX-115 (well 299-W23-19) after the initial leak event

- Repeated occurrences of technetium-99, nitrate, and chromium in downstream groundwater monitoring wells.

From these observations, a less extensive migration of cesium-137 appears to have occurred, and a more extensive migration of mobile constituents apparently occurred relative to the area around tank SX-108. The cesium-137 distribution suggests that *tank* fluid chemistry was not sufficient to radically enhance cesium-137 mobility from the tank SX-115 leak allowing the cesium-137 to migrate with the *tank* fluid. Consequently, no marker remains to indicate the initial distribution of tank fluid in the vadose zone. However, presence of mobile constituents in nearby downgradient wells strongly indicates the tank SX-115 contaminants as the source. Hydraulic forces other than the initial discharge and natural recharge apparently have caused this extensive migration. This supposition is supported by the presence of a water line and a growing cottonwood tree south of tank SX-115 outside of the WMA boundary in the area in the early 1990s. The cottonwood tree supports the theory of sufficient water leakage into the vadose zone over an extended period of time that thereby provided the necessary driving force to push mobile constituents initially discharged to the vadose zone into the unconfined aquifer.

Outstanding features of contamination in the area around tank S-104 include the following:

- High-volume tank S-104 leak
- High cesium-137 concentration zone in one drywell near tank S-104
- Several technetium-99 occurrences downstream of tank S-104 in a series of wells along the east side of the S and SX tank farms
- Several incidents of high rain and snowmelt events coupled with topographic lows on the east side of S tank farm
- One large known water-line failure of 1,892,500 L (500,000 gal) in 1996.

These data are more ambiguous than those available for the other two areas. However, it is postulated that the release and migration pattern here is generally similar to that around tank SX-115 where initially released tank fluid is distributed in the vadose zone and cesium-137 sorbs rapidly on soil and separating from the migrating liquid. Subsequently, technetium-99 is driven to the unconfined aquifer at an accelerated pace due to a combination of tank infrastructure leaks and short-term, high-volume natural precipitation events.

2.1.3 Data Needs

Early in the history of the Tank Farm Vadose Zone Project, project personnel recognized a need to compile existing information concerning all SST farms so that gaps in the state-of-knowledge could be assessed. This study resulted in publication of Jones et al. (1998) in December 1998. This document has served as the basis upon which to build the ongoing data needs to be resolved by the Tank Farm Vadose Zone Project. The document was not developed to address specific regulatory requirements nor was any attempt made to cite regulatory requirements for actions that were assumed to take place in the future.

Areas of investigation and analysis identified in Jones et al. (1998) are ranked in terms of whether or not there was a direct impact to human health or the environment, the current state-of-knowledge, and whether or not the collection of additional data was feasible. The highest-ranking identified elements are listed in Table 2.1. The items listed in Table 2.1 focused primarily on developing a better understanding of contaminant inventory and pertinent soil properties. These primary items have guided the project in the development of DQO and in the design of investigations conducted in the S and SX tank farms.

Table 2.1. Data and Analysis Needs

Item	Rank
Radionuclide and chemical concentration in vadose zone	IA
Leak volumes	IA
Composition of leaked tank waste	IA
Correlation of estimated vs. measured inventory	IA
Projection of contaminant migration	IA
Change in hydraulic properties in contaminated soils	IB
Temperature distribution in contaminated soils	IB

IA: Impact is direct and knowledge level is low; resources should be directed toward implementing activity.

IB: Impact is unclear and knowledge level is low; resources should be directed toward implementing activity.

2.1.4 Data Quality Objectives Process

Using historical information summarized in Jones et al. (1998), the most important data needs for filling in gaps in state-of-knowledge were confirmed in a DQO process (see Figure 2.1).

The data needs for the vadose zone component are summarized in Table 2.2. To some extent, these are the data needed to populate vadose zone models (i.e., two-dimensional cross-sectional models through selected tanks, see Section 4.0). Otherwise, the data are needed to provide confidence in the generalized conceptual model, validate WMA-specific assumptions, and support numerical modeling assumptions. The data type; how it is used (i.e., directly or indirectly); and remarks are provided in Table 2.2.

Figure 2.1. Data Quality Objectives and Data Needs

Based on input from Ecology, DOE, and the DQO process participants, the initial characterization activities in support of the objectives and data needs identified for WMA S-SX are illustrated in Figure 2.1.

Table 2.3 identifies the individuals who were involved in the DQO process between February 16 and April 5, 1999.

Table 2.2. Data Needs to Evaluate Contaminant Flow and Transport Through the Vadose Zone (2 Sheets)

Data Need or Activity	Data Use	Remarks
Refine Vadose Zone Conceptual Model	Provides the basis for the quantitative assessment of impacts to groundwater.	The conceptual model captures and documents the relevant hydrogeology, geochemistry, geologic, and hydrologic processes. It includes the understanding of various contaminant mobility phenomena, infiltration, and sediment parameter values relative to moisture movement, contaminant transport, and contaminant characteristics.
Source Term – The subsurface distribution of CoCs and their chemical characteristics.	Directly used in impact assessment as an initial condition. WMA-specific data are required on the spatial distribution, concentration, and chemical form of the CoCs.	This is sometimes referred to as the 'nature and extent' of contamination. Not possible to adequately describe the source term based solely on WMA-specific data. Source term definition is supplemented by historical leak loss and inventory data.
Stratigraphy – The sedimentary layering, including thickness and orientation, of the various strata and <i>tank</i> farm subsurface infrastructure (e.g., transfer lines and pits).	Directly used in impact assessment as the framework of the vadose zone model. Site-specific data are required to describe stratigraphy.	Large- and small-scale heterogeneities in the subsurface require interpolation between relatively sparse data points. It is not possible to adequately describe the subsurface stratigraphy based solely on site-specific data. Stratigraphy is supplemented with extrapolation from nearby data points and site analogs such as outcrops.
Hydraulic Parameters – The parameters that, together, are used to calculate moisture movement and include soil characteristic curves (e.g., moisture retention, saturated, and matured hydraulic conductivities).	Directly used in impact assessment as vadose zone model input parameters.	Samples from within the WMA are anticipated to be too contaminated to cost effectively perform hydraulic testing. A database of hydraulic parameters has been developed from samples collected elsewhere on the Hanford Site.

Table 2.2. Data Needs to Evaluate Contaminant Flow and Transport Through the Vadose Zone (2 Sheets)

Data Need or Activity	Data Use	Remarks
Transport Parameters – The parameters that, together with moisture movement, are used to calculate contaminant transport and include: molecular diffusion coefficient; longitudinal and transverse dispersivity; bulk density; and geochemical parameters (e.g., contaminant distribution coefficient and contaminant solubility).	Directly used in impact assessment as vadose zone model input parameters.	Samples from within the WMA are anticipated to be too contaminated to cost-effectively determine transport parameters. The contamination also limits the use of in situ tests that might be used in an otherwise uncontaminated area. Extensive laboratory testing of Hanford Site sediments and typical tank waste (e.g., Tc-99, Cs-137, Se-79) has resulted in a large distribution coefficient database, which is a key parameter. Site-specific data will not be available except for contaminant distribution coefficients and bulk density values determined in the laboratory from selected samples.
Infiltration* – The rate at which water enters and percolates through the vadose zone and enters the underlying unconfined aquifer. This includes infiltration from direct precipitation, surface water run on, and water from WMA activities and events such as water-line leaks.	These data are some of the vadose zone model input parameters.	Infiltration is an input parameter that can vary based on conditions (e.g., graveled surface versus interim surface barrier). Hanford Site data exist from simulated current tank farm groundcover conditions and for anticipated surface barriers that could be applied as a part of closure. WMA-specific data will not be available.

Source: **DOERL (2000)**.

*Infiltration is not an independent input. Infiltration is related to the character of the surface, including an engineered barrier and vegetation as well as the topography and the effects run-on, temperature, and the time and rate of precipitation.

CoCs = contaminants of concern.

WMA = waste management area.

Table 2.3. Data Quality Objectives Process Participants

Participant Name	Company	Participant Name	Company
S. Anderson	MACTEC-Meier	K. Lindsey	D. B. Stephens and Associates
S. Blacker	MACTEC, Inc.	Z. Maine-Jackson	Ecology
L. E. Borneman	Fluor Daniel Hanford, Inc.	F. M. Mann*	Fluor Daniel Northwest
H. L. Boston	Lockheed Martin Hanford Corp.	R. G. McCain	MACTEC-ERS
C. R. Cole	PNNL	P. M. McCarthy	Los Alamos Technical Associates
S. J. Coleman	Informatics	D. J. Minter*	Los Alamos Technical Associates
J. D. Crumpler*	Jacobs Engineering Group Inc.	D. A. Myers*	IT Group
S. Dahl	Ecology	D. Olson	DOE Richland Operations Office
R. E. Dav*	CH2M HILL, Inc.	R. W. Ovink*	CH2M HILL Hanford, Inc.
D. Dunning	Oregon DOE	J. A. Poppiti	DOE Richland Operations Office
D. J. Foust*	Lockheed Martin Hanford Corp.	K. D. Reynolds	Waste Management Federal Services
E. A. Fredenburg	Lockheed Martin Hanford Corp.	W. Riggsbee	Yakama Indian Nation
G. W. Gee	PNNL	R. S. Schreiber	Jacobs Engineering Group Inc.
D. Goodman	Montana State University	R. J. Serne*	PNNL
D. Goswami	Ecology	K. Singleton*	CH2M HILL Hanford, Inc.
M. J. Graham	Bechtel Hanford Inc.	R. M. Smith	PNNL
C. J. Grando	Waste Management Federal Services	S. Sobczyk	Nez Perce Tribe
C. C. Haass	Lockheed Martin Hanford Corp.	P. Staats*	Ecology
J. C. Henderson*	Jacobs Engineering Group Inc.	T. L. Stewart	PNNL
R. A. Holten	DOE Richland Operations Office	W. J. Stokes	Lockheed Martin Hanford Corp.
L. M. Johnson*	CH2M HILL Hanford, Inc.	T. Valero	Ecology
V. G. Johnson	PNNL	R. L. Weiss*	CH2M HILL Hanford, Inc.
T. E. Jones*	MACTEC-Meier	R. C. Wilson	CH2M HILL Hanford, Inc.
J. Kelly	MACTEC-Meier	J. Williams	Fluor Daniel Hanford, Inc.
R. Khaleel*	Fluor Daniel Northwest	M. I. Wood*	Waste Management Federal Services
A. J. Knepp*	Bechtel Hanford, Inc. now CHG	R. M. Yasek*	DOE/ORP
J. L. Kovach	Independent Consultant	J. W. Yokel	Ecology
D. C. Larsen	Lockheed Martin Hanford Corp.	J. M. Zachara	PNNL
S. Leja	Ecology*		

Note: Lockheed Martin Hanford Corporation is not CH2M HILL Hanford Group, Inc.

*These individuals participated in both data quality objectives processes.

CHG = CH2M HILL Hanford Group, Inc.

DOE = U.S. Department of Energy.

ORP = Office of River Protection.

PNNL = Pacific Northwest National Laboratory.

2.2 SUMMARY OF WORK PLAN ADDENDA

2.2.1 Overview

The initial field characterization efforts (Henderson 1999) implemented in FY 1999 and FY 2000 included the collection of vadose zone and groundwater data from the following:

- Installation of a new borehole southwest of tank SX-115 (well 299-W23-19)
- Decommissioning of borehole 41-09-39
- Installation of three RCRA groundwater monitoring wells (wells 299-W22-48, -49, and -50).

Ecology and DOE determined that characterization activities should (1) provide data that would support decisions on additional interim measures or ICMs, tank waste retrieval, and tank farm closure and (2) include installation of a new borehole and collection of vadose zone data from new RCRA groundwater monitoring wells. These decisions and the decision by DOE to proceed with the decommissioning of borehole 41-09-39 were the starting point for the DQO process (Henderson 1999). The following summarize the decisions reached by Ecology and DOE based on the DQO process.

- **Decommissioning of borehole 41-09-39** – This borehole was installed as a temporary borehole during two separate drilling campaigns: one beginning in December 1996 in which the borehole was driven to 40.1 m (131.5 ft) with a closed-end steel casing, and one beginning in September 1997 in which the borehole was deepened to 69 m (225.3 ft). Groundwater sampling activities conducted as part of the Hanford Groundwater Program have been completed. The decommissioning activities have been completed, which included introduction of a tracer into the groundwater, borehole geophysical logging, sidewall sediment sampling of selected intervals, and removal of temporary materials and proper sealing of the hole in accordance with *Washington Administrative Code* requirements.
- **Installation of a new exploratory borehole southwest of tank SX-115** – The DQO process resulted in the identification of several potential locations for the proposed new borehole (e.g., near tanks SX-108 and SX-115). DOE and Ecology selected a borehole location southwest of tank SX-115. This location is near a past tank leak. The new borehole, designated 299-W23-19, was installed using a drive-and-drill, dual-wall, reverse air circulation rotary drilling technique. The technique drove conductor casing with staged (telescoping) casings to reduce the likelihood of cross-contamination from penetrating through highly contaminated zones. Split-spoon driven sediment samples and drill cutting samples were collected from about 3 m (10 ft) bgs to just below the water table. The water table was encountered at about 64 m (210 ft) bgs. Selected portions of the samples were analyzed for chemical, radiological, and physical characteristics. A suite of geophysical surveys was performed, and groundwater samples were collected for chemical and radiological analysis. The new borehole was completed as a RCRA-compliant groundwater monitoring well and meets “Minimum Standards for the Construction and Maintenance of Wells” (WAC 173-160) requirements. This new

well is included in the RCRA groundwater monitoring network for routine groundwater sampling and analysis.

- Collection of vadose zone characterization data from RCRA groundwater monitoring wells** – Vadose zone samples were collected during the installation of three RCRA groundwater monitoring wells planned in support of the ongoing RCRA groundwater monitoring effort. The three wells are to replace existing RCRA groundwater monitoring wells because groundwater levels in WMA S-SX are declining by up to 0.6 m/yr (2 ft/yr), and some of the existing monitoring wells are going dry. The southern-most proposed monitoring well (well 299-W22-50) is located about **50 m** (164 ft) southeast of **tank SX-113**. From this well, continuous driven samples were collected from about **6 m** (20 ft) bgs to refusal (near the top of the Ringold Formation). Continuous drill cuttings were collected from refusal to the water table. The other two RCRA groundwater monitoring wells are located east of WMA S-SX. In cooperation with the Hanford Groundwater Vadose Zone Integration Project, continuous drill cuttings were collected and described from one of these two wells. Selected portions of the split-spoon driven samples and cuttings were analyzed for physical, hydraulic, and chemical properties.

The follow-on field characterization efforts (Rogers and Knepp 2000) conducted in FY 2000 included the collection of vadose zone data from (1) installation of a slant borehole beneath tank SX-108 and (2) shallow vadose zone soil investigations in the north end of the S tank farm. The following summarize the field activity decisions reached by Ecology and DOE based on the DQO process.

- Installation of a slant exploratory borehole underneath tank SX-108** – The past leak associated with tank SX-108 and the high radiation content resulted in this tank being identified during the DQO process as the best location for a slant borehole. This borehole was to be installed to the top of the Plio-Pleistocene unit (39.6 m [130 ft] bgs) or maximum depth of contamination, whichever is deeper.
- Shallow vadose zone soil investigation** – This investigation collected sediment samples via direct-push technology in the northern portion of the S tank farm. The shallow investigation consisted of collecting gamma measurements at 8 areal locations from the ground surface and approximately 16.7 m (**55 ft**) bgs. Sediment samples were collected with the direct-push technology from three pushes. The main emphasis was on characterizing unplanned releases within these areas of concern. Three separate areas were characterized: the vicinity of *tank* S-102, the vicinity of *tank* S-104, and the vicinity of the S transfer vault. These sites exhibit separate instances of cesium-137 in vadose zone drywells that may be indicative of near-surface sources. A total of eight push sites were attempted. Two sites met predetermined criteria for sampling and were sampled, providing three samples.

The data collected for both site-specific addenda (Henderson 1999; Rogers and Knepp 2000) included radiological and chemical concentration values for the CoCs including the mobile constituents (e.g., technetium-99 and nitrate) that may impact groundwater and the relatively immobile constituents (e.g., cesium-137) that would impact worker health and safety.

2.2.2 Characterization Locations

The location of the characterization efforts that span from FY 1999 to FY 2000 are shown in Figure 2.2. The figure shows the location for decommissioned borehole 41-09-39 (299-W23-234), new RCRA well 299-W23-19 southwest of tank SX-115, the slant borehole northwest of tank SX-108, and the near-surface characterization effort in S tank farm by tanks S-102 and S-104.

2.2.3 Characterization Techniques

Six distinct techniques were employed in field characterization of WMA S-SX

- Borehole geophysical logging
- Moisture content measurements
- Cone penetrometer-based exploration
- Cable-tool drilling and sampling with side-wall sampling
- Air-rotary drilling and sampling
- Percussion-driven drilling and sampling.

Each technique was applied to provide specific samples or information meeting project needs that were either identified in Myers (1997), Henderson (1999), or Rogers and Knepp (2000) or later identified as important for understanding the physical or chemical processes at work in the vadose zone. Improvements in drilling technology sponsored by this activity allowed safe and efficient sample collection in the high radiation zone beneath tank SX-108. Other improvements aided the programs in a variety of areas.

2.2.3.1 Borehole Geophysical Logging. Spectral gamma logging was performed on all available boreholes within WMA S-SX (DOE-GPO 1996, 1998, 2000a, 2000b). These logs provided the basis for work conducted. Logging consisted of measurements taken with one of two sondes; a 35% high-purity intrinsic germanium sonde was the standard. In zones where contamination levels rendered this tool ineffective, a high-rate (low-efficiency) high-purity intrinsic germanium sonde was deployed. Measurements were generally taken as 200-second counts at 15 cm (0.5 ft) intervals.

Analysis of historical gross gamma logging records (Myers 1999; Myers et al. 1999) identified several boreholes in WMA S-SX where changes in the gamma flux were taking place.

2.2.3.2 Moisture Content Measurements. Measurement of soil moisture content was not included in the preliminary work plan (Henderson 1999). The distribution of moisture content in the southern portion of the SX tank farm (Myers 2001c) was determined to be an important piece of information leading to determining sources of recharge. Moisture content measurements were taken with a neutron moisture probe instrument (i.e., 503DR Hydroprobe®) that was calibrated to the steel casing sizes common to the tank farm. Measurements were taken at 30 cm (1 ft) intervals from a maximum depth of 44 m (133 ft) to ground surface. Sixteen-second counts were used.

Figure 2.2. Waste Management Area S-SX, Location Map of Characterization Activities, Surrounding Facilities, and Wells

Note: All wells are preceded by 299-.

2.2.3.3 Cone Penetrometer-Based Exploration. Two cone penetrometer-based devices were deployed around tanks S-102 and S-104. The primary tool was a sodium-iodine-based gross/spectral gamma system. The secondary tool was a sampling tool. A series of pushes were made in regions determined through the Spectral Gamma Program (DOE-GJPO 1997) to potentially be contaminated due to tank losses or piping leaks. Calibration of the system is documented in *Calibration of the Cone Penetrometer Gamma Probe* (Myers 2001a) and results documented in *Cone Penetrometer Tests with Gross and Spectral Gamma at the S-Tank Farm, 200 West Area, Hanford Site, Richland Washington* (Myers 2001b).

2.2.3.4 Cable-Tool Drilling and Sampling. Cable-tool drilling was used to advance borehole 41-09-39 (299-W23-234) from 43 m (132 ft) to total depth. Both drive-barrel and hard-tool techniques were used. During decommissioning of the borehole a sidewall sampling device was deployed using a work-over rig operating as a cable-tool system.

2.2.3.5 Air-Rotary Drilling and Sampling. Air-rotary drilling was used to advance well 299-W23-19 from ground surface to total depth. Near continuous sampling was accomplished using the down-hole air hammer to advance split-spoon samplers into the formation. Once the sampler had been retrieved to the surface, the borehole was reamed to full diameter and the drill casing advanced to maintain the hole. Extensive efforts were taken to control discharges from this system. These efforts included double-encasing the discharge hose, diverting the hose through a cyclone to capture the coarsest materials, and then routing all air through an entrained filtration system (i.e., Torit®) to remove fine-grained material. Finally, all exhaust air was routed through a high-efficiency particulate air filtration system. The cyclone and Torit® were further contained inside a sealed, limited-access tent.

2.2.3.6 Percussion-Driven Drilling and Sampling. A specially constructed percussion drilling machine and sampling system was employed to advance the slanted borehole (299-W23-64) beneath tank SX-108. The purpose of this system was to collect samples from the very highly contaminated region beneath an SST. No drill cuttings were brought to the surface as the hole was driven. Driving force was transmitted from a 1,814 kg (4,000 lb) diesel pile driver through the outer casing and an inner drill string. Once the drill string reached a predetermined sample depth the inner string was removed, which opened the end of the outer casing to the formation. An internally shielded split-spoon sampler was then attached to the inner drill string centered in the drive casing and lowered to the sampling horizon. The sampler was then driven into the formation using the diesel hammer. The inner string was extracted and the sampler detached and prepared for shipment. The drive-head was reconnected to the inner string, lowered to the bottom of the bore, and the process repeated. All contaminated materials were handled remotely by a mechanical arm.

2.2.4 Deviations from Waste Management Area Addenda

Deviations from the two work plan addenda and the activity plan for WMA S-SX (Henderson 1999; Rogers and Knepp 2000; Myers 1997) were documented as approved Engineering Change Notices issued against the original documents. By updating the plan in this manner, there were no true deviations from the planned work. There were, however, moderate differences between how the work was originally planned and how the work was actually accomplished for two tasks: borehole 41-09-39 and the SX-108 slant borehole. There were no deviations for the other three

tasks (i.e., borehole 299-W23-19, RCRA groundwater wells, or the shallow soil investigations). The following sections summarize the deviations encountered at borehole 41-09-39 and at the SX-108 slant borehole.

2.2.4.1 Borehole 41-09-39 (299-W23-234). Borehole 41-09-39 was originally driven from the surface to 40.1 m (131.5 ft) using a closed-end casing. The borehole was then extended to a depth of 68.6 m (225 ft) using the cable-tool method to drive sampling devices and casing. After the bore reached groundwater a temporary screen was set, a series of groundwater samples were collected, and tests were conducted to provide information on the unconfined aquifer. The borehole was decommissioned and vadose zone soil samples were collected from the upper 40.1 m (131.5 ft) of the borehole.

Some of the water used to cool the milling tool while cutting the heavy wall casing was lost to the formation. The original design of the casing shoe for the 11.4 cm (4.5 in.) casing called for a flush outside surface. Friction buildup against the casing increased the force required to drive this casing to the point where advancement was not possible. The casing was removed from the bore and a more standard, under-reaming casing shoe was deployed. Minimal carry-along took place following this change.

A change was implemented to carry out a test using borehole 41-09-39 as an injection site for sodium-bromide tracer.

Decommissioning of the lower portion of the borehole went according to plan (Henderson 1999). However, several changes were necessary to decommission the upper portion of the bore. Additional cuts of the heavy wall casing were needed to enable the casing to be removed. The first cut was to remove the casing drive shoe and the second was to overcome an apparent bend in the casing. Sections of casing were grouted in place.

Changes in implementing laboratory analyses were also made. The work plan (Henderson 1999) called out specific samples to be analyzed. As the borehole extension progressed, it became evident that more information would be garnered if the samples to be selected for detailed analyses were selected based on the screening analyses performed on every sample. The samples for detailed analyses were selected by a group representing Ecology, DOE, and Tank Farm Vadose Zone Project personnel and subcontractors.

Changes to the original work plans for extending and decommissioning borehole 41-09-39 were communicated to Ecology via formal Engineering Change Notices made to work plans and by including personnel in meetings and discussions where selections of which samples to be analyzed for what constituents were made.

2.2.4.2 SX-108 Slant Borehole (299-W23-64). The surface location of the SX-108 slant borehole was established based on the intended target zone beneath the tank, the surface and subsurface infrastructure of the farm, and the restrictions on how close to the base of the tank the borehole would be allowed to pass. Ground-penetrating radar was used to map and confirm the locations of subsurface utilities. From a three-dimensional map the surface location was selected.

This borehole was advanced at an angle 30° from vertical passing approximately 3 m (10 ft) from the base of tank SX-108. Ten samples were called out in the work plan for this effort (Rogers and Knepp 2000); that number was increased to 17 to more fully characterize this environment. One of the 17 samples was lost from the sampler during drilling, but 16 were successfully recovered. The borehole was advanced to a depth of 43.9 m (144 ft) vertically, 52.2 m (171.2 ft) absolute distance (Sydnor 2000). The last sample collected was from the fine-grained sediments of the undifferentiated Hanford formation/Plio-Pleistocene unit silty sands.

The borehole was geophysically logged and subsequently decommissioned. Because the driven casing could not be successfully cut, the final decommissioning was carried out under a variance granted by Ecology.

The analytical scheme developed in conjunction with Ecology was significantly altered. The analytical program developed early in the planning of this work was designed to be the same as that applied to boreholes 41-09-39 and 299-W23-19. Based on the lessons learned from those efforts, many of the analyses that would have been conducted during the second or third phases were run during the initial phase. Sharing of samples with the S&T activity of the Hanford Groundwater Vadose Zone Integration Project has resulted in an extensive suite of analyses being run that were not part of the planning document.

The number of intervals sampled was increased to ensure that critical zones of interest were not overlooked. Because sampling could only take place at 1.5 m (5 ft) intervals, bypassing zones where potentially significant information could be gathered was determined to be inappropriate. The analytical scheme was changed to take advantage of the information collected during preceding characterization efforts and to make most efficient use of laboratory resources. The S&T activity, with its access to research facilities across the nation, expressed keen interest in the knowledge to be gained from these unique samples. Because of this interest, the sum of information to be gained has been exponentially expanded.

Because the changes increased the level of effort and increased the amount of information to be gained from this portion of the work plan, only oral notification of the changes was made. Formal documentation of the changes associated with decommissioning were made and written confirmation of these alterations received.

2.3 INTEGRATION WITH OTHER PROJECTS

Other projects from the Hanford Site as well as from offsite have contributed significantly to this document. Because much of the effort was actually made inside the tank farm fences, the active support of RPP Tank Farm Operations staff was crucial to success. Much of the information gathered during these tasks will not only affect the RCRA Corrective Action Program activities performed by the Tank Farm Vadose Zone Project, but will also support the activities needed for SST retrieval and closure. Other projects (e.g., Hanford Groundwater Program, 200 Area Remedial Action Project, the Hanford Groundwater Vadose Zone Integration Project, and projects supported by DOE Headquarters) contributed during the planning and often provided specialized analyses.

2.3.1 River Protection Project Tank Farm Operations

The CHG Tank Farm Vadose Zone Project worked with the RPP Tank Farm Operations to ensure that characterization activities were conducted safely, within the bounds of established procedures, and fit within the authorization basis (Goetz 1999).

Work to be performed within the bounds of any tank farm is planned in accordance with nine CHG enhanced work plan procedures. Once the scope of work is established in an approved work plan, the details of how, where, and who will do the work are further defined through the enhanced working plan process. The end result of an enhanced working plan process is a work package that defines all elements of a piece of work. A draft work package is often prepared and then presented to those individuals who will be directly involved as well as representatives from Radiological Control, Health and Safety, Authorization Basis, and management.

To the extent possible, for the work described by this report a single work crew was assigned. Continuity of the work crew contributed significantly to the successful completion of in-farm work.

2.3.2 River Protection Project Single-Shell Tank Retrieval and Closure Project

The CHG Tank Farm Vadose Zone Project worked with the RPP SST Retrieval and Closure Project to ensure appropriate data were collected to aid in waste retrieval decisions. Various meetings were held with SST Retrieval and Closure Project personnel to ensure information obtained during the field investigation could be incorporated into planned SST waste retrieval operations. The sharing of information assists the waste retrieval program in establishing the appropriate retrieval technologies and in setting criteria for leak detection, monitoring, and mitigation strategies.

The past leak model results were incorporated into the ongoing retrieval performance evaluation modeling effort for S tank farm (Thompson 2001) to ensure consistency among the two programs. Although there are differences in the duration of analysis (i.e., 1,000 vs. 12,000 years), the information for the past leak source term used in the retrieval performance evaluation for S tank farm is the same as presented in Section 4.0 and Appendix E.

2.3.3 Hanford Groundwater Project

The Hanford Groundwater Project is responsible for monitoring and remediation (where necessary) of the groundwater at the Hanford Site.

2.3.3.1 Geological Investigation. Both the Hanford Groundwater Project and the Tank Farm Vadose Zone Project have interest in the role of the geologic system in controlling the movement of contaminants. The Tank Farm Vadose Zone Project has participated in ensuring that at least one new monitoring well being drilled through the Hanford Groundwater Project is sampled in a near-continuous manner at each WMA. Adjacent to WMA S-SX, the Tank Farm Vadose Zone Project has participated in the sampling of three such wells.

2.3.3.2 Completion of Borehole 41-15-08 as Monitoring Well 299W-23-19. The vadose zone characterization borehole adjacent to tank SX-115 was advanced, per the work plan

(Henderson 1999), into the groundwater to permit one-time sampling of that medium under the Hanford Groundwater Project. Analytical results from that groundwater sample showed significant technetium-99 contamination to be present. A decision was made to convert the test borehole to a RCRA-compliant groundwater monitoring well so that this occurrence could be monitored over time. Personnel have been trained in tank ~~farm~~ entry procedures to permit the well to be sampled.

2.3.3.3 Sampling and Tracer Test in Borehole 41-09-39. Borehole 41-09-39 was made available to the Hanford Groundwater Project for sampling and testing before it was decommissioned. The groundwater in this borehole was essentially free of contaminants. This well exhibited the highest levels of vadose zone contamination known to date when the sampling was accomplished. The high contamination was present predominantly in the upper regions of the vadose zone. The borehole presented an opportunity to directly measure the rate and direction of groundwater movement beneath the WMA. A groundwater tracer test using sodium-bromide was proposed, planned, and implemented. Because groundwater movement is only about 50 m/yr (164 ft/yr), the tracer has not yet reached the nearest downgradient groundwater monitoring wells. Additional reasons for not reaching downgradient groundwater monitoring wells include change in groundwater flow direction, uncharacterized heterogeneity, and well screen locations.

2.3.4 200 Area Remedial Action Assessment

Interaction with the 200 Area remedial investigation/feasibility study work in adjacent cribs included sharing and review of work plans, site conditions description report, and ~~data~~ that became available as work progressed. Work in and around the tank farms conducted by the RPP is ahead of work scheduled to be done under the Environmental Restoration Program.

2.3.5 Hanford Groundwater Vadose Zone Integration Project

The work reported in this FIR was done with full cooperation and input from the Hanford Groundwater Vadose Zone Integration Project. Progress reports were made through the DOE Headquarters-mandated Integration Project Expert Panel, convened by the Integration Project as well as through other public meetings hosted by the Integration Project. Input from this body of experts was used to help guide the direction taken by the Tank Farm Vadose Zone Project. In addition, the Integration Project offered numerous opportunities to enhance the investigation beyond the requirements of the accepted work plans, thus expanding the state-of-knowledge upon which decisions will be made. The following sections outline contributions from specific organizations within the Hanford Groundwater Vadose Zone Integration Project.

2.3.5.1 Science and Technology Activity. The S&T activity of the Integration Project is an important aspect of the team effort that produced this document. The following outline some of the S&T activity functions.

- **Liaison with DOE Headquarters-Funded Efforts.** Samples collected during drilling of the characterization and RCRA-supported boreholes were made available to researchers in the Environmental Management Sciences Program for additional analyses.

- **Enhanced Analyses.** In addition to DOE Headquarters funding, the Integration Project funded enhanced analyses of the samples from the characterization and RCRA-supported boreholes. Appendix D summarizes much of the important efforts.
- **Advanced Modeling.** Although the modeling done by the Tank Farm Vadose Zone Project was relatively complex, some effects (e.g., thermal, transient chemical effects) are not included. The S&T activity investigated the impacts of such effects. Appendix D summarizes much of their important efforts.
- **Inventory Modeling.** As part of the effort to understand the Hanford Site inventory as a whole, the inventory modeling activity reinvestigated the process knowledge of tank waste transfers and, importantly, what the inventory of tanks were at the times of potential leakage. These efforts are described as part of the inventory effort.
- **Venue for Presenting Results.** Cooperation with the S&T researchers provides a venue by which individual research efforts are presented through a variety of media, including peer-reviewed journal articles. This wider audience and availability for outside review increases the technical acceptance of the entire program.

2.3.5.2 Input to System Assessment Capability. The System Assessment Capability Project is intended to provide the means by which the impact of all Hanford activities can be assessed. One of the potential impacts on the Columbia River and the surrounding environment is the inventory of wastes lost from the SSTs over the 50-year operating history of the Hanford Site. Direct and frequent interaction with the developers of the System Assessment Capability has been and will continue to be an important focus of the Tank Farm Vadose Zone Project.

2.3.5.3 Expert Panel Review. The Integration Project's panel of experts provided continuing review and advice on how to optimize the value of information gathered during the field investigation. Data derived from the investigation were scrutinized by the panel and the panel provided independent interpretations of those data; this level of review helped to ensure that all reasonable explanations for the findings were considered.

2.3.5.4 Public Interactions. The Integration Project provides a variety of venues where the public can learn about tank farm activities. Two public meetings a month are normally held. Additional special meetings (e.g., with the Oregon Office Of Energy) are often held.

2.3.6 DOE Headquarters-Funded Activities

Through the Environmental Management Sciences Program, DOE Headquarters has funded a number of researches to study vadose zone issues. Many of these researches are taking advantage of using the soil samples taken from this characterization effort to perform advanced analyses. A summary of some of these activities is provided in Appendix D.

3.0 INVESTIGATIVE RESULTS AND CONCLUSIONS

The WMA S-SX field investigation included the following activities:

- Installation of a RCRA-compliant groundwater well southwest of tank SX-115
- Installation of an exploratory slant borehole beneath tank SX-108
- Sediment sampling and decommissioning of borehole 41-09-39
- Shallow vadose zone soil investigation around tank S-104
- Collection of vadose zone characterization data from the installation of three RCRA groundwater monitoring wells (299-W23-48, 299-W23-49 and 299-W23-50).

The major investigation findings are summarized as follows.

- Radiologic and chemical analyses of water extract samples of soils were taken from three characterization boreholes in the SX tank farm (299-W23-19, 41-09-39, and SX-108 slant borehole) with depth. Similar analyses were also done for soils from two RCRA boreholes (299-W22-48 and 299-W22-50) that were not exposed to tank fluids. Comparison of these analyses for tank farm versus non-tank farm soils shows elevated concentrations of several constituents in the tank farm borehole soils that are attributed to tank fluid leakage (primarily tanks SX-115 and SX-108) into the soil column. The set of tank leak constituents includes technetium-99, cesium-137, chromium, and nitrate. With the exception of cesium-137, high concentration depth intervals were observed in all three boreholes, primarily in the lower subunits of the Hanford formation (H1 and H2) and the upper Plio-Pleistocene unit (PPlz). In these high concentration depth intervals, technetium-99 ranged from 95,000 to 237,000,000 pCi/L; chromium ranged from 3 to 218,000 mg/L; and nitrate ranged from 6,000 to 994,000 mg/L. High cesium-137 concentrations were found in the two boreholes contaminated by the tank SX-108 leak (41-09-39 and SX-108 slant borehole). High cesium-137 concentration ranges occurred in subunits H1 and H2 between 125,000 and 95,700,000 pCi/g.
- Groundwater samples have been collected from monitoring wells adjacent to WMA S-SX including 299-W23-15, 299-W23-19, 299-W22-48, 299-W22-49, 299-W22-50, 299-W22-80, 299-W22-81, and 299-W22-82 beginning in the early 1990s. Most recently published values are provided in Appendix C, Section C.7 from Johnson and Chou (2001). Also unpublished data are available in the Hanford Environmental Information System database. Collectively, maximum concentrations of 81,500 pCi/L, 220 mg/L, and 562,000 µg/L for technetium-99, chromium, and nitrate were measured. Of these well data, a strong indication of tank leak waste sources is found only at well 299-W23-19 next to tank SX-115. In this well, the highest technetium-99 concentrations (up to 81,500 pCi/L) have been measured and currently the concentration values have reduced to 36,000 pCi/L (September 2001). Maximum values for all three contaminants exceed current drinking water standards (900 pCi/L for technetium-99, 50 µg/L for chromium, and 45,000 µg/L for nitrate).

- The bulk of the matric potential measurements for sediments from four boreholes in and around WMA S-SX suggest a draining soil profile. Because no site-specific recharge measurements are available, estimates of natural recharge are based primarily on other Hanford Site measurements (e.g., lysimeter studies). These data suggest that recharge in the tank farms under current conditions can be as high as 100mm/yr (4 in./yr). Recharge also appears to have occurred as a result of manmade events (e.g., water-line leaks, particularly near tank SX-115). Recharge rates from these events are highly uncertain and quantitative estimates are not available.
- Improvements in drilling technology sponsored by this activity allowed safe and efficient sample collection in the high radiation zone underneath SX-108. Other improvements aided the programs in a variety of areas (Section 2.2).

Because the investigative results (particularly soil and groundwater data near tank SX-115) suggest that manmade water sources have accelerated contaminant migration (Section 3.4.2), interim measures (Section 3.5) have been initiated to minimize the infiltration from manmade sources. These measures include capping monitoring wells, cutting water pipelines, and building berms around the S and SX tank farm boundaries.

Section 3.1 provides the geology and hydrology information collected or interpreted from the field investigation activities. Section 3.2 provides the geochemical information collected or interpreted from the field investigation activities. Section 3.3 provides the nature and extent of contamination for the soils and groundwater data sampled and analyzed from the field investigation activities. Section 3.4 provides the conceptual model based on the preceding three sections. Section 3.5 discusses interim measures and ICMs as being conducted or planned in FY 2001 and 2002.

3.1 HYDROGEOLOGIC CONDITIONS

Geologic and hydrologic characteristics of the Hanford Site and local areas within the Hanford Site (e.g., WMA S-SX) have been extensively studied. In this section the results of those studies, both regional and site-specific, are summarized. More detailed discussion of the geologic and hydrologic characteristics of the WMA S-SX vadose zone and unconfined aquifer are provided in Appendix C, Sections C.4.0 and C.5.0, respectively. Geologic cross-sections used in numerical modeling and impact assessment (Section 4.0) are included in Appendix E.

3.1.1 Geology

The Hanford Site is located within the Columbia Plateau of Southeastern Washington State. This broad plain, situated between the Cascade Mountains to the west and the Rocky Mountains to the east, is underlain by a thick sequence of Miocene age tholeiitic basalt flows (the Columbia River Basalt Group). These basalt flows have been folded and faulted, creating broad structural and topographic basins, separated by asymmetric anticlinal ridges. Sediments of late Miocene, Pliocene, and Pleistocene age have accumulated up to 518 m (1,700 ft) thick in some of these basins. The Hanford Site lies within one of the larger of these basins, the Pasco Basin. This basin is partially bisected by the Umtanum-Gable Mountain anticline creating two subordinate synclinal basins. The largest of these is the Cold Creek syncline, which is further subdivided into two basins, the Wye Barricade depression and the Cold Creek depression. The Cold Creek depression underlies the principal WMAs (200 East and 200 West Areas) of the Hanford Site. The generalized stratigraphy beneath the Hanford Site consists of, in ascending

order, the Columbia River Basalt Group, the Ringold Formation, the Plio-Pleistocene unit, and the Hanford formation (Figure 3.1). Thin veneers of Holocene alluvium, colluvium, and eolian sediments discontinuously overlie these principal geologic units.

The **WMA S-SX** stratigraphic characteristics are shown by a northeast-to-southwest cross-section across the **SX tank farm** (Figures 3.2 and 3.3). The **S** and **SX tank farms** were constructed into the upper Hanford formation sediments underlying the 200 West Area, along the north limb of the Cold Creek syncline, which exists just west of **WMA S-SX** and is oriented generally north to south. Stratigraphic units in the vadose zone underlying or adjacent to these **tank farms** (in descending order) include backfill materials and naturally occurring Hanford formation sediments, the Plio-Pleistocene unit, and the Miocene- to Pliocene-age Ringold Formation. Because these units are part of the synclinal structure, there is a general tendency for these units to dip west to southwest in this area. The water table lies in the Ringold Formation, and the unconfined aquifer is located entirely in the Ringold Formation.

The Hanford formation sediments are divided into three subunits in **WMA S-SX**. In descending order, the subunits are **H1a**, **H1**, and **H2**. Their characteristics are described as follows.

- **Subunit H1a** – Comprised predominantly of interstratified slightly silty, medium to very fine sands (Figure 3.3), ranging in thickness from 0 m (0 ft) where it was removed during excavation of the **S** and **SX tank farms**, to about 9 to 12 m (30 to 40 ft) to the southwest (Figure 3.3). The top of this unit dips slightly (approximately 2°) to the southwest.
- **Subunit H1** – Comprised primarily of a gravel to gravelly sand intercalated by coarse sand (Figure 3.3) that appears to correlate beneath the **SX tank farm**. This sequence ranges in thickness from 1 m (3 ft) to nearly 10 m (30 ft) beneath the **S tank farm**. Sobczyk (2000) reports subunit **H1** to be thickest beneath **tank S-102** (Figure 3.4) where coarse-grained flood deposits backfilled an apparent channel eroded into the top of the underlying subunit **H2**. This subunit is also notable because of its high cesium-137 content in the area south and west of **tank SX-108**.
- **Subunit H2** – Comprised predominantly of silty fine sand that ranges in thickness from about 24.3 m (80 ft) east of the **SX tank farm** to approximately 10.7 m (35 ft) west of the **tank farm** (Figure 3.5). Johnson and Chou (1998) suggests that this thinning may signify some scouring on top of the subunit, perhaps associated with a secondary flood channel, similar to the north-south trending flood channel that bisects Cold Creek bar (Figure 3.6). The top of this subunit generally dips about 6" to the southwest, with some local relative highs and lows present throughout. The base of this subunit is indicated by a diagnostic increase in total gamma activity on borehole geophysical logs.

The Plio-Pleistocene unit sediments are divided into two distinct facies in **WMA S-SX**, subunits **PPlz** and **PPlc**, in descending order. Subunit **PPlz** is characterized by an abundance of silt interstratified with fine sand and clay. Subunit **PPlc** is characterized by an abundance of pedogenic calcium-carbonate cement, often in multiple carbonate-cemented zones. Calcium-carbonate contents do not exceed 10 wt% in the **SX tank farm** boreholes evaluated in the **WMA S-SX** field investigation. The combined total thickness of the Plio-Pleistocene unit is up to 13.1 m (43 ft) in the vicinity of the **SX tank farm** (Figure 3.5). Subunit **PPlz** is relatively thick (up to 10.7 m [35 ft]), compared to subunit **PPlc**, which measures only 1 to 4 m (4 to 13 ft) in thickness.

Figure 3.1. Generalized, Composite Stratigraphy for the Late Cenozoic Sediments Overlying the Columbia River Basalt Group on the Hanford Site

Sources: Johnson and Chou (1998); Johnson and Chou (1999).

Figure 3.2. SX Tank Farm and Vicinity Showing Location of Borehole 299-W23-19

Note: Location of cross-section A-A', represented in Figure 3.3.

Figure 3.3. Hydrogeologic Cross-section of the Vadose Zone Beneath the SX Tank Farm

Figure 3.4. Fence Diagram of Vadose Zone Stratigraphy Underlying Waste Management Area S-SX"

*The top sand layer corresponds to subunit H1a. Gravel Unit B is subunit H1 and the next three lower units (sand, Gravel Unit A, and sand) comprise the subunit H2.

Figure 3.5. Elevation Maps of Stratigraphic Unit Tops Underlying Waste Management Area S-SX*

*Elevation contours in subgraphs A and C mark the bottom of subunits H1 and H2.

Figure 3.6. Digital Elevation Model Map of a Portion of the Pasco Basin Showing Routes and Facies Distributions for the Last Pleistocene Cataclysmic Floods

The Ringold Formation lies directly on top of the Columbia River Basalt Group and is approximately 125 m (410 ft) thick beneath the S and SX tank farms. A relict erosional and weathered surface occurs at the top of the Ringold Formation beneath the SX tank farm and dips to the southwest beneath that tank farm. The northwest-southeast trending trough-shaped surface appears to conform to an ancestral Cold Creek channel and drainage system that developed following late Pliocene incision of the Ringold Formation, and prior to early Pleistocene cataclysmic flooding, during the period between approximately 2 to 3 million years ago. The Ringold Formation locally consists of three principal stratigraphic units (see Figure 3.1):

- Fluvial gravels of Unit A
- Fine-grained, paleosol-lacustrine sequence referred to as the lower mud unit
- Fluvial gravels of unit E.

Ringold unit E contains the main unconfined aquifer beneath 200 West Area.

In addition to the primary stratigraphic units described, clastic dikes may be present in the WMA S-SX vadose zone. Although clastic dikes have been observed in numerous locations around WMA S-SX, none have been observed in the WMA S-SX vadose zone itself. Clastic dikes are vertical to near-vertically oriented sedimentary structures that cut across horizontal bedding planes. The dikes have been observed in all types and ages of geologic materials found beneath the Hanford Site including basalt; interbed sediments; the Ringold Formation; and the sands, mud, and gravels of the Hanford formation (Fecht et al. 1999). Clastic dikes are especially notable within the sand- and silt-dominated facies of the Hanford formation where they have been observed to be a few centimeters to more than a meter thick and extend to depths of 36 m (120 ft) bgs or more.

3.1.2 Hydrology

Tank leaks occur under variably saturated conditions, making natural recharge from meteoric water (from winter precipitation and snowmelt), artificial recharge from operations-related sources, and vadose zone hydrology important drivers for contaminant movement to groundwater. Recharge, vadose zone, and groundwater conditions for WMA S-SX are briefly discussed in the following sections.

3.1.2.1 Recharge. S and SX tank farm surfaces are covered with gravel to prevent vegetation growth and provide radiation shielding for site workers. Bare gravel surfaces, however, enhance net infiltration of meteoric water, compared to undisturbed, naturally vegetated surfaces. Infiltration is further enhanced in the tank farms by the effect of percolating water being diverted by an impermeable, sloping surface of the tank domes. This umbrella effect is created by the 23 m (75 ft) inside diameter buried tank domes. Water, shed from the tank domes, flows down the tank walls into underlying sediments. Sediments adjacent to the tanks, while remaining unsaturated, can attain elevated moisture contents (Kline and Khaleel 1995). Enhanced infiltration from a gravel-covered tank dome can provide potential for faster transport of contaminants to the water table. In addition, other sources of recharge include unintentional surface spills, infiltration of surface runoff from leaking water lines, and ancillary tank-related equipment.

Natural recharge can vary greatly depending on factors such as climate, vegetation, surface condition, and soil texture. Studies conducted at the Hanford Site suggest that recharge rates can vary from less than 0.1 mm/yr (0.004 in./yr) on a variety of soil and vegetative combinations to greater than 130 mm/yr (5.1 in./yr) on bare basalt outcrops or bare, gravel-covered waste sites (Gee et al. 1992). Data from experimental sites such as the Field Lysimeter Test Facility and the prototype Hanford barrier, both in the 200 East Area, suggest that recharge through gravels can vary from 15% to 70% of precipitation, with the lower amount occurring under vegetated conditions (Gee et al. 1993; Fayer and Walters 1995; Fayer et al. 1996; Gee et al. 1996). With a long-term annual average precipitation of 160 mm (6.3 in.), the higher percentage translates into a recharge rate of about 100 mm/yr (4.0 in./yr) and was observed on clean gravels that were kept free of vegetation. Drainage from bare sands is about 70 mm/yr (2.8 in./yr) under Hanford Site climatic conditions (Ward et al. 1997). However, there has been no direct measurement of recharge on tank farm gravels, which are known to contain a larger amount of fines than clean gravels. Thus, it is entirely possible that the tank farms experience a recharge rate that ranges between that observed for bare sand and clean gravels (Ward et al. 1997).

Recharge estimates based on environmental tracer techniques (Prych 1995; Murphy et al. 1996) are generally consistent with those based on lysimeter studies. However, the tracer techniques, while powerful, are not applicable to disturbed sites such as the tank farms. **Also**, these techniques have been unable to measure significant recharge at sites with coarse soils and shallow-rooted vegetation, because of deep percolation of natural tracer at these sites.

Soil matric potential is often used as an indicator for deep drainage (recharge) conditions. However, it should be noted that, while matric potentials can provide useful information about the variability of recharge across WMA S-SX, they cannot discern differences in contribution to recharge from natural and artificial sources.

Matric potential measurements are available for sediments from four boreholes (Serne et al. 2001a, 2001b, 2001c):

- RCRA boreholes 299-W22-48 and 299-W22-50 outside of the SX tank farm
- Contaminated borehole 41-09-39 near tank SX-109
- Contaminated borehole 299-W23-19 near tank SX-115.

The matric potential measurements for the 10 sleeves from borehole 299-W23-19 are relatively high (sediments relatively wet) throughout the sediment profile, and the measurements suggest a draining profile. Unit gradient conditions persist throughout the profile. Serne et al. (2001b) postulates that a recharge estimate of 50 to 100 mm/yr (2.0 to 4.0 in./yr) would not be inconsistent with the measured matric potentials for borehole 299-W23-19 samples. However, it should be noted that it is more likely that an artificial source, rather than meteoric recharge, is responsible for the high matric potential values at borehole 299-W23-19 near tank SX-115. There is a huge depression south of tank SX-115 and an 8-in. water line running directly south of the tank. Water lines are prone to leaks and the depression south of tank SX-115 provides an excellent location for collection of water from water-line leaks. In fact, a cottonwood tree has grown in this area (Johnson and Chou 1998). This, combined with the upward trend of technetium-99 in borehole 299-W23-19 directly west-southwest of tank SX-115, provides circumstantial evidence that the matric potential data for borehole 299-W23-19 are more of a

reflection of artificial than natural recharge. (The technetium-99 concentration in borehole 299-W23-19 increased from 39,000 pCi/L in October 1999 to 81,500 pCi/L in March 2001.)

For the two RCRA boreholes outside of the SX tank farm (299-W22-48 and 299-W22-50), it appears that at 30 m (100 ft) bgs, the measured matric potentials are low (the sediments are relatively dry), compared to sediments in the contaminated borehole 299-W23-19. Unlike borehole 299-W23-19, matric potential data for the two RCRA borehole sediment samples do not suggest unit gradient conditions (Seme et al. 2001a). However, matric potential data for sediment samples from the upper horizon do indicate that meteoric recharge (or recharge from man-made sources) has penetrated to a depth of at least 30 m (100 ft) bgs at the two RCRA borehole sites. Below that depth, sediments from these two RCRA well sites are significantly drier, compared to those from the contaminated borehole 299-W23-19. This suggests that the wetting front has not penetrated the lower horizons and non-equilibrium conditions persist below 30 m (100 ft) bgs.

Lysimeter studies (Gee et al. 1992) suggest that sediments kept free of vegetation can cause accelerated drainage. Such conditions are believed to exist at the two RCRA borehole sites. With the disruption caused by the initial construction of the tank farms in the late 1950s, one could assume that there has been nearly 40 years of elevated drainage resulting from the severe disturbance and vegetation removal. It is clear that, at a disturbed site such as the RCRA borehole sites where vegetation has been removed, equilibrium is altered and non-equilibrium conditions can persist for quite some time.

Unlike matric potential data for samples from borehole 299-W23-19 near tank SX-115, measurements from borehole 41-09-39 samples near tank SX-109 show considerable variability. While the majority of the data are indicative of a draining profile, a number of measurements suggest an upward flow (Serne et al. 2001c). Seme et al. (2001c) attributes this to the drying effect resulting from the heat load from high-heat tank SX-108. Given the large variability of the measured matric potentials for the 30 samples and the lack of unsaturated hydraulic properties for the SX tank farm sediments, it is not possible to estimate the magnitude of deep drainage (recharge) at this borehole site.

For the purposes of field investigative report modeling, a base case recharge estimate of 100 mm/yr (3.9 in./yr) is used. Such an estimate is similar in magnitude to measured drainage rates from gravel surfaces kept free of vegetation (Gee et al. 1992). For simulations involving tank farms with an interim barrier, a recharge rate of 0.5 mm/yr (0.02 in./yr) is used. This is based on experimental data from a prototype Hanford barrier that has been designed and built in 200 East Area to limit recharge to less than 0.5 mm/yr (0.02 in./yr) (DOE-RL 1999a). This is also supported by the numerical simulation results in Smoot et al. (1989) where it is reported that with a relatively impermeable barrier over the tank farm, the drainage to a 2 m (7 ft) backfill depth decreased to less than 0.5 mm/yr (0.02 in./yr) after 8 years for cases of either a backfill or a clean graveled surface.

The closure barrier for tank farms is assumed to be an enhanced RCRA Subtitle C barrier with a design life of 500 years. The recharge through such a barrier is estimated to be 0.1 mm/yr (0.004 in./yr) (Fayer et al. 1999). For a degraded closure barrier, recharge rates are expected to return to predevelopment conditions (i.e., the same as a shrub-steppe ground cover) with a

recharge estimate of 3.5 mm/yr (0.14 in./yr). Such an estimate is within the range of values reported in Fayer and Walters (1995). Table 3.1 summarizes the timeline estimates for barrier emplacement at the S and SX *tank* farms and the corresponding recharge estimates.

Table 3.1. Timeline Estimates for Emplacement of Interim and Closure Barriers at the S and SX Tank Farms and Corresponding Recharge Estimates

Condition Simulated	Recharge Estimate (mm/yr)
No barrier [years 2000 to 2010]	100
Interim barrier [years 2010 to 2040]	0.5
Closure barrier (design life 500 yrs) [years 2040 to 2540]	0.1
Degraded closure barrier (after 500 yrs) [years 2540 to 3000]	3.5

3.1.2.2 Vadose Zone Hydrology. Because water movement is the primary mechanism for radionuclide and chemical transport, an objective of the **WMA S-SX** field investigation was to evaluate the potential for radionuclide and chemical transport beneath the tank farms by considering the nature and distribution of flow within the vadose zone. In general, two types of moisture movement can occur in the vadose zone beneath the tank farms.

- **Piston flow** – Uniform moisture movement through the soil matrix whereby infiltrated water displaces initial water (wetting-front infiltration). Under piston-like flow conditions most, if not all, preexisting water ('old' water) is displaced and moved ahead of the 'new' infiltration water added from above this zone. Under natural recharge conditions, the medium- to coarse-grained sands at tank farm sites are expected to be quite conducive to piston flow.
- **Preferential flow** – Process whereby water and contaminants move along preferential pathways. Preferential pathways can be natural (e.g., clastic dikes) or anthropomorphic (e.g., unsealed monitoring wells). While preferential flow has been recognized and widely studied under saturated or near-saturated flow conditions (Nkedi-Kizza et al. 1983; De Smedt and Wierenga 1984), there is little evidence of it in arid and semiarid climates or under low water fluxes, particularly where soils are coarse-grained such as those under *tank* farms. Thus, under natural recharge conditions, precipitation at arid sites is usually too low to invoke preferential flow; much of the water in the *dry* soils is simply adsorbed onto the grain surfaces and cannot move along preferred pathways.

Other potential preferential pathways during tank leaks include wetting front instability or 'fingering' flow. Wetting front instability, reported in petroleum-related literature, is a special case of interface instability during immiscible fluid displacement in porous media. The phenomenon is triggered by unfavorable differences between the viscosities and densities of two fluids across their interface—a condition that can potentially exist during tank leaks.

Among potential preferential pathways, the probability of a tank encountering a clastic dike is substantial. For example, numerous clastic dikes occur at the US Ecology site southwest of the 200 East Area that may serve as conduit for preferential flow. While a clastic dike can potentially increase flow rate, it is less likely to intersect large segments of leaked wastes, and when it does the cross-sectional area of the intersection is small (DOE-RL 1997b). Therefore, presence of clastic dikes in unsaturated media appears unlikely to contribute much to the transport to groundwater of the bulk quantity of leaked tank wastes. Nonetheless, as described in Appendix E, the clastic dike effects are included in modeling.

A field study in the 200 East Area south of the Plutonium-Uranium Extraction Plant demonstrated the effect of geologic heterogeneities on water contents in a natural arid setting (Sisson and Lu 1984). The observed higher water contents were strongly correlated with fine soil layers, which have a higher water-holding capacity than coarse soils. In addition, the observed profiles were remarkably similar for the 15-year interval between measurements at the field site (Fayer et al. 1995). This suggests that, in the absence of artificial recharge, the 'natural' moisture contents of the sediments are essentially determined by the nature of geologic heterogeneity, and the vadose zone water content profiles are at quasi-equilibrium with the natural recharge rate. This is also demonstrated by the moisture content profiles in RCRA boreholes 299-W22-50 and 299-W22-48 (Seme et al. 2001a) and contaminated boreholes 41-09-39 (Seme et al. 2001c), 299-W23-19 (Seme et al. 2001b), and 299-W10-196 (Freeman-Pollard et al. 1994) near tank T-106. The measured water contents are much higher in the Plio-Pleistocene unit than in the Hanford formation.

The dominance of lateral movement is a unique feature of unsaturated flow, especially in an arid setting (Yeh et al. 1985a, 1985b). Horizontal stratification enhances such movements, because at high tension (i.e., dry soil) hydraulic conductivities of fine-textured materials are relatively high and the fluid prefers to spread laterally in the fine media than to move vertically through the coarse media. Such a phenomenon is referred to as moisture-dependent anisotropy and can potentially be a dominant mechanism for lateral flow. This has important implications for vadose zone contaminant transport from tank leaks. For example, measurements of vadose zone contamination at the SX tank farm (DOE-GPO 1996b) and the tank T-106 leak (Routson et al. 1979) suggest significant lateral movement. As described in Appendix E, moisture-dependent anisotropy effects are included in modeling.

A description of geologic heterogeneities as well as soil hydraulic properties (i.e., moisture content versus matric potential and unsaturated hydraulic conductivity versus moisture content relationships) is needed to evaluate the storage and flow properties of tank farm soils. Furthermore, assessing the ability of the vadose zone to act as a buffer requires properly accounting for conditions whereby the tank leak chemistry itself may affect physical and hydraulic properties of the soil and therefore the mobility of contaminants.

No site-specific data on soil moisture characteristics are available for vadose zone sediments in the S and SX tank farms. However, several data catalogs exist on physical and hydraulic properties for sediments in the 200 and 100 Areas (Khaleel and Freeman 1995; Khaleel et al. 1995; Khaleel and Relyea 1997; Khaleel 1999; Khaleel et al. 2000; Khaleel and Relyea 2001). As part of other Hanford Site projects, particle-size distribution, saturated hydraulic conductivity, moisture retention, and unsaturated hydraulic conductivity data have

been collected in the vicinity of the S and SX tank farms. Sediment samples were collected in the vicinity of the Environmental Restoration Disposal Facility, tank T-106, and operable units 200-UP-1 and 200-UP-2 in the 200 West Area. Also available are physical and hydraulic properties data for the sandy gravel sediments in the 100 Area along the Columbia River (Khaleel and Relyea 2001). These samples were used as surrogates to represent the hydraulic properties for the gravel-dominated sequence at the S and SX tank farms. Details are provided in the WMA S-SX FIR modeling data package (Khaleel et al. 2000). The data used in modeling are summarized in Appendix E. Appendix E also provides effective (upscaled) values of flow and transport parameters for the vadose zone at the S and SX tank farms.

3.1.2.3 Groundwater Conditions. The water-table map for March 2000 (Hartman et al. 2001) indicates that the direction of groundwater flow in the southern portion of the 200 West Area is primarily toward the east, with a slight southeastern component. The natural flow pattern in this area was altered by the formation of groundwater mounds created by the discharge of large volumes of wastewater at disposal facilities. The southeastern trend is more apparent in the area of the decommissioned U pond. These mounds are declining, and groundwater flow is gradually returning to pre-Hanford conditions. The water table is gradually declining at the rate of approximately 0.6 m/yr (2 ft/yr), which may result in a future shift to a more easterly direction and decreased flow rates as the gradient declines.

The unconfined aquifer in WMA S-SX resides in partially cemented Ringold Formation sands and gravels. The cementing is not present at greater depths. This may result in a more transmissive aquifer in the future as the water table continues to decline.

Hydraulic conductivities based on slug tests for RCRA wells 299-W22-48, 299-W22-49, and 299-W22-50 cover a range of 1.55 to 8.2 m/day (0.5 to 27 ft/day) (Johnson and Chou 2001). Such a range brackets the averaged, large-scale hydraulic conductivity estimate used in the Hanford Site-wide groundwater model for the WMA S-SX region (Appendix E). Estimates for effective porosity, based on tracer test analysis, range between 0.068 and 0.257 (Johnson and Chou 2001); such a range falls within that usually reported for semi-consolidated to unconsolidated alluvial aquifers of 0.05 to 0.30, and again brackets the large-scale value used in the Hanford Site-wide groundwater model (Appendix E). Hydraulic gradient, based on tracer test analysis, is about 0.002 whereas the groundwater velocity ranges from 0.013 to 0.374 m/day (0.04 to 1.2 Wday) (Johnson and Chou 2001).

3.2 GEOCHEMICAL CONDITIONS

Geochemical conditions in WMA S-SX are determined by in situ undisturbed vadose zone characteristics, the chemistry of leaked tank fluids, and the interactions between fluids and the soil-soil water system. Because tank fluids of varying composition were distributed over parts of the vadose zone at various times, geochemical conditions affecting contaminant and other constituent behavior vary, temporally and spatially. The effect of these variable conditions on contaminant mobility is of key interest. This section focuses on those aspects of vadose zone geochemistry that influence contaminant migration. The four contaminants of interest identified by these studies are cesium-137, technetium-99, chromium, and nitrate.

A substantial database has been developed to quantify past and current geochemical conditions in contaminated areas in WMA S-SX. The majority of data used to understand geochemical conditions are soil sample and soil water analyses from boreholes drilled in contamination areas inside the SX tank farm and in nearby relatively undisturbed zones (see Appendix B for detailed discussion). *Also*, laboratory studies and analyses focused on mechanisms controlling contaminant migration (see Appendix D for detailed discussion) provide useful insights. Geochemical conditions are of greatest interest in soils contaminated by the tanks SX-107, SX-108, SX-109, and SX-115 leaks. Because the tank leak fluid chemistry has some significant differences that have affected contaminant migration, geochemical conditions are discussed separately for each contamination area as well as the undisturbed area east of WMA S-SX.

3.2.1 Undisturbed WMA S-SX Vadose Zone Soil Geochemical Conditions

Two RCRA groundwater monitoring wells (299-W22-48 and 299-W22-50) were drilled on the east side of WMA S-SX where vadose zone soils have not been subjected to tank leaks. The soils analysis database (Serne et al. 2001a) shows a standard set of soil minerals (primarily quartz, feldspars, and minor amounts of smectite, illite, chlorite, kaolinite, and calcite) and particle-size distribution typical of the stratigraphic units in this area. Cation exchange capacity varies between 6 and 40 meq/100 g depending on the procedure used.

For the most part, soil water chemistry derived from 1:1 extracts is fairly consistent throughout the soil column. The pH values in both boreholes fall into a normal range (7 to 8.5) except at 18 to 21 m (60 to 68 ft) bgs in borehole 299-W22-50 where elevated pH values (about 10 and 9) are measured. The reason for this increase is not clear. Primary anions are nitrate, chloride, and sulfate concentrations. Other than slight enrichment of nitrate and sulfate in Plio-Pleistocene subunit PPlc, the profiles are undistinguished.

Water extract cation concentrations as a function of depth are listed for borehole 299-W22-48 in Appendix B, Table B.21 and graphed in Appendix B, Figure B.28. Appendix B, Table B.22 provides cation concentrations for borehole 299-W22-50. Primary cations are sodium, magnesium, potassium, and calcium. Generally, total anion concentrations are 50 to 60 mg/L. In both boreholes slight elevations of calcium and natural strontium occur in subunit PPlc because of the relatively high quantities of calcium carbonate (40 wt%). A slight unexplained calcium enrichment anomaly occurs at 18 m (60 ft) bgs in borehole 299-W22-50.

3.2.2 Tanks SX-107, SX-108, SX-109 Vadose Zone Soil Geochemical Conditions

Soil samples from two boreholes near tanks SX-107, SX-108, and SX-109 were collected and analyzed. The SX-108 slant borehole was drilled beneath tank SX-108 to collect samples as close to the leak point from the tank and beneath the tank, a location that had not been previously sampled. Borehole 41-09-39 lies about 20 m (66 ft) southwest of tank SX-108, and soils from this borehole represent a location far enough removed from the tank leak point to demonstrate the effects of lateral movement on tank fluid distribution in the vadose zone.

Based on the presumed volumes leaked and gamma radiation measurements taken in many drywells, the tank SX-108 leak is considered to be the primary source of tank waste contamination in borehole 41-09-39 and the SX-108 slant borehole. Estimates of tank fluid

chemistry (Section 3.3; Appendix C, Section C.3.0; and Appendix D, Section D.7.3) that had a dominating impact on local chemical conditions and contaminant mobility are extremely high pH, and extremely high cesium-137, sodium, aluminum, and nitrate concentrations.

High cesium-137 concentrations in the upper subunits of the soil column (17 to 26 m [55 to 86 ft bgs]) in both boreholes (Appendix B, Sections B.2.0 and B.4.0) indicate that cesium-137 was highly mobile initially, essentially migrating with the tank fluid for some limited time. This pattern of cesium-137 migration is rarely seen in Hanford Site soils.

Extensive laboratory experiments (Appendix D, Section D.3.0) clearly demonstrate the importance of competition for sorption sites between cesium-137 and sodium and show that estimated tank fluid composition was suitable for favoring sodium versus cesium-137 sorption, thereby mobilizing cesium-137. The current distribution of tank fluid constituents in the soil column also explains why cesium-137 is currently fairly immobile. Geochemical conditions have changed over time as tank fluid has migrated and continued to interact with the soil column. Water extract data in soil columns from both boreholes show a distinct chromatographic separation of cesium-137 and sodium with depth. Once cesium-137 and sodium were sufficiently separated, cesium-137 sorption became favorable, fixing it in place. Empirical sorption data, estimated by ratioing cesium-137 concentrations in water extractions versus total concentration based on gamma logging data, show increasing sorption with decreasing sodium concentrations.

Little data exist, suggesting that nitrate behavior is affected either by tank fluid chemistry, the soil-soil water system, or chemical interactions between them. Consequently, the vertical extent of tank fluid migration in both boreholes is indicated by nitrate concentration profiles with depth. The profiles in both boreholes indicate that tank fluids have not penetrated beyond the Plio-Pleistocene unit. The borehole soil sample analyses show that technetium-99 concentration profiles generally match well with nitrate showing that technetium-99 is also essentially unreactive with solids. Therefore, past and present in situ geochemical conditions have no real affect on their mobility.

Chromium mobility apparently has been slightly influenced by geochemical reactions. High chromium concentration zones are slightly shallower than high technetium-99 zones, indicating occurrence of a small degree of retardation and chemical interaction for chromium species. Over time, interactions between tank fluid and the soil column have created a combined porewater chemistry characterized by intermediate pH values and total dissolved solids concentrations. Laboratory tests and chromium species characterization (Appendix D, Section D.4.0) indicate that the limited retardation of chromium in the soil column has occurred because iron(II)-bearing minerals reduce chromium from the VI to the III valence state which allows sorption or co-precipitation to occur. Chromium(III) was also measured in soil samples. The results also indicate that highly caustic solutions dissolved iron(II)-bearing minerals, thereby facilitating the kinetics of chromium reduction.

3.2.3 Tank SX-115 Vadose Zone Soil Geochemical Conditions

Soil samples from borehole 299-W23-19 just southwest of tank SX-115 were collected. Geochemical conditions in this borehole, based on soil water extract data, are generally similar to those in borehole 41-09-39 and the SX-108 slant borehole. Soil water extract compositions show

a moderate pH with zones of higher concentrations of tank fluid constituents (nitrate, sodium, and technetium-99) at different depths in the soil column. The significant exception is that there are only trace quantities of cesium-137 at tank bottom depth in this borehole. This difference is readily explained by the initial tank fluid composition estimates (Table 3.2), which show a much more dilute solution with much reduced cesium-137 and sodium content. Because of this initial condition, insufficient competition for sorption sites occurred, and cesium-137 sorbed very quickly into soil as the tank fluid leaked from the tank.

Table 3.2. Summary of Selected Tank Supernate/Salt Concentrations at Time of Leak

Tank	S-104	SX-107	SX-108	SX-109	SX-110	SX-111	SX-112	SX-113	SX-114	SX-115
Assumed Leak Date	1965	Ave. 1964-1967	Ave. 1965-1966	Ave. 1964-1967	1974	1973	1969	1962	1972	1964
Chemicals	(mole/L)	(mole/L)	(mole/L)	(mole/L)	(mole/L)	(mole/L)	(mole/L)	(mole/L)	(mole/L)	(mole/L)
Sodium	8.7E+00	1.9E+01	2.0E+01	1.5E+01	6.1E+00	5.3E+00	1.3E+01	8.0E+00	8.9E+00	3.6E+00
Aluminum	1.6E+00	3.3E+00	3.4E+00	2.6E+00	7.3E-01	5.3E-01	2.2E+00	1.3E+00	9.7E-01	8.3E-01
Chromium	1.6E-01	3.9E-01	4.1E-01	3.2E-01	6.8E-02	5.9E-02	2.1E-01	1.7E-01	1.0E-01	5.1E-02
Nitrate	3.0E+00	4.9E+00	5.5E+00	4.5E+00	1.7E+00	1.5E+00	3.5E+00	2.8E+00	2.5E+00	1.2E+00
Nitrite	1.6E+00	4.5E+00	4.4E+00	3.2E+00	1.3E+00	1.1E+00	3.1E+00	1.3E+00	1.9E+00	7.8E-01
Radionuclides	(Ci/L)	(Ci/L)	(Ci/L)	(Ci/L)	(Ci/L)	(Ci/L)	(Ci/L)	(Ci/L)	(Ci/L)	(Ci/L)
Technetium-99	4.2E-05	2.4E-04	2.3E-04	1.6E-04	1.6E-04	2.1E-04	1.6E-04	4.4E-05	2.9E-04	2.9E-05
Cesium-137	1.2E-01	8.4E-01	7.7E-01	5.2E-01	1.27E-01	5.8E-02	5.3E-01	1.3E-01	1.4E-01	9.9E-02

The relative positionings of nitrate, technetium-99, and chromium are similar to those shown in borehole 41-09-39 and the SX-108 slant borehole. Nitrate and technetium-99 are concentrated at the bottom of the tank-fluid-soil-interaction zone at the Plio-Pleistocene unit, and the high chromium zone occurs at a shallower depth. As before, it is concluded that nitrate and technetium-99 are essentially unaffected by geochemical conditions and partial reduction of chromium has occurred, aided by higher pH tank fluids.

3.3 NATURE AND EXTENT OF SUBSURFACE CONTAMINATION

A reasonable understanding of the nature and extent of subsurface contamination in WMA S-SX is required to complete transport modeling and risk calculations (Section 4.0 and Appendix E). Initially, this understanding was developed through extensive reviews of historical records and integration of data from previous field investigations. In this characterization effort, additional and complementary studies were completed to improve estimates of WMA S-SX vadose zone contamination, including the following:

- Additional inventory estimates derived from the historical records of tank operations
- Kriging analyses to determine cesium-137 distribution and total inventory
- Speciation analyses using thermodynamic concepts

- Analysis of soil samples contaminated by tank waste taken from exploratory boreholes in the SX tank farm.

Results of these studies, summarized in the following sections, provide a consistent correlation between theoretical inventory estimates and field measurements of vadose zone Contamination. This observation improves confidence that tank inventory estimates are reasonable source term estimates for flow and transport modeling and risk evaluation.

The current WMA S-SX field investigations have not addressed the near-surface contamination that resulted from routine tank farm operations. The current state of understanding of near-surface contamination is found in Appendix B, Section B.6.0.

3.3.1 Tank Leak Inventory Estimates

The importance of developing quantitative inventory estimates for tank waste materials lost to the soil column during leak events was fully appreciated during development of the technical basis for the current SST vadose zone characterization program (Jones et al. 1998). The impacts for a given contaminant are proportional to the amount of contaminant in the soil column and thus to the initial amount of the contaminant lost from the tanks. As noted in the discussions of cesium-137 migration in the vadose zone in Section 3.2.2, the rate of movement of contaminants in the soil column may be impacted by other co-contaminants. Therefore, the goal was to develop reasonably complete inventories for tank wastes lost to the vadose zone.

The approach for developing inventory estimates has focused on combining leak volume estimates with waste composition estimates (Jones et al. 2000a). The development of tank leak inventory estimates was made possible by a number of recent SST waste investigations. Efforts to develop current tank waste inventory estimates led to both a compilation of tank waste transfer records (Agnew et al. 1997) and a model providing current inventory estimates in all Hanford Site SSTs and double-shell tanks (Agnew 1997). These models have been used to predict inventories of tank wastes at times of suspected leaks and proposes an approach for estimating leak volumes for high-heat tanks (Agnew and Corbin 1998).

The long-term gross gamma logging (Myers 1999; Myers et al. 1999) and more recent spectral gamma logging data (DOE-GJPO 1996, 1998, 2000a, 2000b) have provided by far the best overall understanding of the nature and extent of gamma-emitting radionuclide contamination in the SST farms. Analysis of the gamma logging data and other soil analysis data provided quantitative estimates of cesium-137 contamination in the SX tank farm vadose zone (Goodman 2000; Sullivan et al. 2001). The development of work plan addenda for WMA S-SX was greatly enhanced by a number of expert panel reports (DOE-RL 1997b; DOE-RL 1999d) and supporting documents (Johnson et al. 1999). As described in the following sections, information gleaned from these sources provided a basis for developing preliminary inventory estimates for most known tank leaks in the 12 SST farms (Jones et al. 2000a; Jones et al. 2000b; Corbin et al. 2001; Jones et al. 2001). Although the discussion focuses on the WMA S-SX field investigation results, this broader perspective provides a better basis for developing conceptual models for tank leak events. As constrained by the available modeling programs, the initial tank-leak inventory estimates were provided on a total elemental and curie basis (with the exception of a few anions such as chloride and nitrate).

A more complete understanding of the long-term impacts of tank leaks on the vadose zone environment requires specific knowledge of chemical species present in the leaked tank waste. Two speciation-modeling analyses of the materials lost from tanks in WMA S-SX have been completed (Appendix D, Section D.7.3; Jones et al. 2000a). The speciation modeling results provide (1) a better understanding of the bounding conditions for REDOX boiling-waste system operations and (2) guidance for geochemical modeling required to better understand radionuclide and chemical migration in the vadose zone.

Section 3.3.1.1 describes the present understanding of tank waste composition at the time of a tank leak. Building on the gamma logging data (Section 3.3.1.2) and on soil data analyses (Section 3.3.4), the amount and distribution of cesium-137 leaked into the soil is determined (Section 3.3.1.3). Knowing the tank waste composition and the amount of tank waste leaked, estimates of all the major contaminants are derived and presented (Section 3.3.1.4). Speciation is described in Section 3.3.2. The results are summarized in Section 3.3.3.

3.3.1.1 Waste Composition Estimates. There has long been an interest in using flowsheet data from various Hanford Site chemical processes coupled with waste transfer records to develop tank waste inventory estimates (Jungfleish 1984). Researchers at Los Alamos National Laboratory, supported by many individuals associated with the Hanford tank waste characterization program (Agnew 1997) brought the approach developed by Jungfleish to fruition. The Los Alamos National Laboratory task involved two major activities.

- The extensive waste transfer records were centralized into a single document, *Waste Status and Transfer Record Summary (WSTRS Rev. 4)* (Agnew et al. 1997).
- Flowsheet information was coupled with an understanding of the chemistry of each waste stream to develop estimates of solid and liquid compositions for each waste stream.

The composition of each major waste stream was coupled with the waste volumes for each of the transfers into and out of each Hanford Site waste tank. Using simple waste mixing rules for the sum of waste transfers through individual tanks, current waste compositions and total inventories were calculated for each Hanford Site waste tank. This approach is termed the Hanford defined waste (HDW) model (Agnew 1997). The HDW model develops two waste composition estimates:

- Sludge composition, estimated by the tank layering model
- Supernate composition, estimated by the supernatant mixing model.

The waste composition estimates from the supernatant mixing model module are a combination of liquid and salt cake (Agnew 1997).

Although the driver for the HDW model was to develop 'current' tank inventory estimates, the HDW model provides the capability for developing inventory estimates at any point in time in each tank. As noted above, the HDW model results for selected SX tank farm high-heat tanks are used in Agnew and Corbin (1998) to develop the 'Hanford leak model,' which projects preliminary leak volume estimates for tanks SX-108, SX-109, SX-111, and SX-112. The Agnew and Corbin (1998) approach for developing tank composition estimates at specific points in time was used in estimating tank leak events in WMA S-SX (Jones et al. 2000a) and in other WMAs

(Jones et al. 2000b; Corbin et al. 2001; Jones et al. 2001). Table 3.2 contains the waste composition estimates for selected contaminants for the 10 tanks in the S and SX tank farms thought to have leaked (see major discussion in Jones et al. 2000a). Complete waste composition estimates for those 10 tanks are listed in Appendix C.

Complete waste compositions can be coupled with leak volumes to develop leak inventory estimates. However, published leak volume estimates (Hanlon 2001) are highly uncertain for a number of the SX tank farm leaks (Jones et al. 2000a). **Thus**, it was necessary to use other data sources to develop leak volume estimates. This process is discussed in the following sections.

3.3.1.2 Gamma Logging Data. Since the early 1960s gamma logging data have been used as a secondary tank leak monitoring system (Isaacson and Gasper 1981). In practice, strategically placed shallow boreholes (24 to 46 m [80 to 150 ft] bgs), called ‘drywells,’ were routinely monitored for changes in total gamma activity. Hence, the activity is known as gross gamma logging. Drywells were located approximately 3.1 m (10 ft) from the tanks and generally 4 to 8 drywells surrounded each ‘active’ tank (that is, leak monitoring concentrated on tanks currently being used to store liquid wastes). Tanks known to have leaked (e.g., tank SX-113) where all pumpable liquids had been removed, were not given high priority to be monitored for additional leakage. For additional leak monitoring capability, 10 of the 15 tanks in the SX tank farm had laterals (i.e., horizontal pipes radiating from a central caisson) installed approximately 3.1 m (10 ft) below the base of the tank. Except for tank SX-113, each tank had three laterals radiating from a nearby caisson. As the prototype for laterals as the tank leak monitoring system, tank SX-113 had five laterals installed under it.

During the routine gross gamma logging program, changes in gamma activity in a borehole would suggest potential leakage from a nearby waste storage tank or waste transfer line. Although the gross gamma logging data were stored electronically from **1974** to the end of the logging program in 1994, data comparisons within any specific drywell were restricted to short time intervals. Gross gamma logging data were treated as being of value only for ‘real-time’ leak monitoring of active SSTs.

As part of the WMA S-SX vadose zone characterization, historic gross gamma logging data are assessed in Myers (1999) and Myers et al. (1999). Although the gamma logging instrumentation underwent major modifications (particularly the probes) over the 20 years of data collection, the data exhibited surprising reproducibility as shown in stack plots (Myers et al. 1999). The data analysis also provided useful information about the potential movement of gamma emitting radionuclides over the 20-year period.

The validity of gross gamma logging methodology as a tank leak detection system was critically evaluated in *A Scientific Basis for Establishing ~~Dry~~-Well Monitoring Frequencies* (Isaacson and Gasper 1981). One of the conclusions from the evaluation was that the gross gamma data provided far more insight into the migration of radionuclides in the soil than it did about potential leaks in active tanks. With the passage of time and thus decay of the short-lived mobile gamma emitting radionuclides (e.g., ruthenium-106) the 1981 conclusions are more valid than ever.

In 1994 a baseline spectral gamma-logging program was initiated to assess the nature and extent of gamma emitting radionuclides in the tank farms vadose zone (DOE-GJPO 1995a, 1995b, 1995c; DOE-RL 1996) by using the unique radiation emitted to identify and quantify the radionuclides. Essentially all existing drywells within each tank farm were logged with a system designed to provide specific isotopic composition of gamma-emitting radionuclides. Baseline spectral gamma logging results were published for each tank farm. The gamma-logging probe selected for the initial logging runs became saturated at approximately 1,000 pCi/g of cesium-137. Thus, in the most highly contaminated zones, quantitative values were not determined. At a later date the highly contaminated zones were re-logged using a less sensitive probe and updated results were published in supplemental tank farm reports. Ninety-eight drywells were logged in the SX tank farm and results were published in *Vadose Zone Characterization Project at the Hanford Tank Farms, SXTank Farm Report* (DOE-GJPO 1996) and its supplement, *Addendum to the SXTank Farm Report* (DOE-GJPO 2000b). Seventy-two drywells were logged in the S tank farm; results are published in DOE-GJPO (1998) and its supplement, *Addendum to the S Tank Farm Report* (DOE-GJPO 2000a).

The baseline spectral gamma-logging program has made major contributions to the current tank farm vadose zone characterization efforts. The main radionuclide found was cesium-137. Only very small amounts (i.e., a few pCi/g) of cobalt-60 and/or europium-154 were found in the S and SX tank farms.

3.3.1.3 Kriging Analysis. The SX tank farm gamma logging and soil analysis data for cesium-137 represent 'point measurements' along a vertical, horizontal, or slant direction. The goal of kriging analysis of the cesium-137 data was to establish mathematically defensible inventory estimates associated with the gamma contamination around each tank in the SX farm. Two separate data analyses were conducted. The first, conducted by Professor Dan Goodman, Montana State University (MSU) beginning in 1998, combined gross gamma and spectral gamma logging data with soil analysis data from borehole 41-09-39 and historical soils data (Raymond and Shdo 1966; Goodman 2000). The MSU results are referred to as 'MSU kriging results' in this document. The second statistical analysis of the SX tank farm cesium-137 data, conducted by HydroGeologic, Inc. (HGL) (Sullivan et al. 2001), began with the same data set as used by MSU but also included newly acquired soils analysis data from the SX-108 slant borehole (Serne 2001d) and the updated spectral gamma logging results (DOE-GJPO 2000b).

The MSU statistical analysis focused on two objectives

- The gross gamma logging data were evaluated to establish calibration curves so as to use the gross gamma data to develop 'datapatches' for the regions of the spectral gamma data set lost because of detector saturation in the initial spectral gamma logging.
- The resulting enhanced gamma logging-based cesium-137 data set was coupled with soils analysis data to develop cesium-137 inventory estimates for the regions around each tank in the SX farm.

The projected cesium-137 inventory estimate for each tank in the SX tank farm is listed in Table 3.3. Inventory estimates are reported at both the 50 and 95 percentiles.

Tank	MSU 50% (pCi)	MSU 95% (pCi)	HGL 50% (pCi)
SX-101	9.1E+09	2.1E+10	2.3E+10
SX-102	0.0E+00	0.0E+00	1.5E+10
SX-103	0.0E+00	0.0E+00	2.1E+10
SX-104	2.7E+08	1.6E+09	7.7E+09
SX-105	5.5E+09	1.3E+10	1.3E+10
SX-106	0.0E+00	0.0E+00	5.9E+09
SX-107	8.0E+15	1.5E+16	4.2E+16
SX-108	1.4E+16	3.6E+16	3.9E+16
sx-109	7.2E+14	2.3E+15	1.6E+15
sx-110	2.0E+12	1.3E+13	7.5E+12
sx-111	2.3E+11	1.1E+12	2.3E+11
sx-112	1.8E+13	9.5E+13	2.9E+13
SX-113	0.0E+00	0.0E+00	6.4E+07
SX-114	0.0E+00	0.0E+00	1.9E+08
SX-115	N/R	N/R	1.1E+14

*Includes surface spills.

HGL = HydroGeologic, Inc.

MSU = Montana State University.

N/R = not reported.

The second kriging analysis was focused on understanding the impact of the addition of the cesium-137 soils analysis data from the SX-108 slant borehole investigation on the overall cesium-137 inventory estimate. Also included in the second kriging analysis were the updated spectral gamma logging data for cesium-137 from highly contaminated zones (DOE-GJPO 2000b). Thus, the data patches from historical gross gamma data developed by MSU for that kriging analysis were not required for the HGL kriging analysis.

The first step in any kriging process is the development of a variogram model. Vertical and horizontal correlation lengths are determined during the variogram analysis. Significantly different correlation lengths were reported between the two kriging analyses.

- MSU variogram analysis led to a horizontal correlation length of 8.2 m (27 ft) and a vertical correlation length of 3 m (10 ft)
- HGL variogram analysis led to horizontal and vertical correlation lengths of 15 m (49 ft) and 20 m (66 ft), respectively.

The practical result of longer Correlation lengths is the projection of somewhat larger plume volumes with the existing data set.

There are a number of reasons for the large correlation lengths reported in the HGL kriging analysis (Sullivan et al. **2001**). The most obvious reason is the addition of the cesium-137 concentrations along the SX-108 slant borehole, giving much better definition of the vertical contamination directly below *tank* SX-108. However, there were also differences in approach. The MSU variogram analysis treated all of the available data within the SX tank farm while the HGL variogram analysis focused on the area around *tank* SX-108. The decision to estimate correlation lengths using data only from around *tank* SX-108 focused the analysis in the area where the maximum amount of data was available. The correlation lengths derived from the analysis of data around *tank* SX-108 were then used in the kriging analysis for all of the SX tank farm data. The intent was to apply the knowledge gained from detailed field investigations around *tank* SX-108 to the contamination found around and under other SX farm tanks. This was justified because very similar waste types leaked from all failed SX farm tanks and the geology was assumed to be reasonably similar across the SX tank farm. The HGL kriging analysis also reports results of sensitivity studies associated with data processing decisions.

Both kriging analyses used data compression techniques to reduce the size of the data set prior to computations because the data set was too large to be processed with available computer systems. Both groups separated the tank farm area into a 1 m by 1 m (3.3 ft by 3.3 ft) grid size. MSU used a 1 m (3.3 ft) depth to form 1 m³ (35 ft³) sections. The geometric mean of all cesium-137 concentration values within the 1 m³ (35 ft³) was assigned to the point at the center of the cube. The variogram analysis and kriging were completed with this reduced data set. The HGL data process approach was quite similar except the grid size was 1 m by 1 m by 0.5 m (3.3 ft by 3.3 ft by 1.6 ft). Intuitively, reducing the grid size will better reflect the original data.

The cesium-137 inventory estimates developed in the HGL kriging analysis are also listed by *tank* in Table 3.3. **An** example of the graphical representation of cesium-137 activity generated in the HGL kriging analysis is shown in Figure 3.7. Graphical representations of cesium-137 activity at other concentrations are found in Appendix C.

The cesium-137 inventory estimates reported by HGL are the mean values. The cesium-137 inventory estimates reported by HGL and listed in Table 3.3 are most directly comparable to the 50 percentile data reported by MSU and listed in Table 3.3.

Figure 3.7. Plan and Cross-Section View of Cesium-137
Contaminated Soil Above 5×10^3 pCi/g

The geometric mean is commonly used as an approach for compressing large environmental data sets, where values span multiple orders of magnitude (e.g., the spectral gamma logging data in the SX tank farm). However, other approaches could be taken. For example, a more conservative approach would be to assign the data value of the volume space as the maximum value reported within that grid volume. As a sensitivity study, HGL completed a kriging analysis using 'maximum' values rather than geometric means. As expected, the cesium-137 inventory estimates were somewhat higher (by a factor of about two) using the 'maximum' values. Sensitivity study results are included in Appendix C and in the HGL kriging analysis report (Sullivan et al. 2001).

A comparison between MSU and HGL cesium-137 inventory estimates near and under SX farm tanks are shown in Table 3.3. The only major difference in cesium-137 inventory estimates between the two studies involves tank SX-107. Although the HGL kriging analysis results suggest the cesium-137 inventory lost from tank SX-107 to be slightly larger than the total quantity of cesium-137 lost from tank SX-108, the volume of contaminated soil associated with tank SX-107 is less than half of the volume of contaminated soil associated with tank SX-108. The HGL kriging analysis results for tank SX-107 are driven by gamma logging data from the three laterals. One lateral is projected to have cesium-137 activity at levels close to 8.0×10^8 pCi/g. With the larger correlation lengths calculated by HGL for tank SX-108 and applied to other tanks in the SX tank farm, this particularly highly radioactive lateral strongly influences overall cesium-137 inventory estimates for tank SX-107. It appears the tank SX-107 cesium-137 inventory estimate is likely an artifact of the data handling methodology. Resolution of this issue will likely require re-logging of the laterals under tank SX-107 with a calibrated spectral gamma tool.

3.3.1.4 Inventory Estimates for WMA S-SX Tank Leaks. Leak volume estimates and selected inventory estimates for WMA S-SX tank leaks are listed in Table 3.4. The complete data set is available in Appendix C and Jones et al. (2000a). Leak inventory estimates for tanks SX-107, SX-108, and SX-109 were based on cesium-137 inventories developed by the MSU kriging analysis (Goodman 2000). Leak volumes for these three tanks were estimated from cesium-137 inventory estimates (Goodman 2000) coupled with waste composition estimates. Inventory estimates for tanks S-104, SX-113, and SX-115 were based on documented leak volumes (Jones et al. 2000a; Hanlon 2001). For these three cases, leak volumes were combined with tank waste inventory estimates (see Appendix C, Section C.3.0) to develop inventory estimates for each tank leak.

This discussion will focus on potential modifications to the published WMA S-SX inventory estimates based on the updated HGL kriging results.

The inventory estimates shown in Table 3.4 for tanks SX-107, SX-108, and SX-109 were developed using 95 percentile cesium-137 data from MSU (Goodman 2000). That is, these inventory estimates reported in Jones et al. (2000a) were biased high by using the 95 percentile data rather than the mean or 50 percentile values. The decision to use the higher values was driven by an assumption that the cesium-137 plume estimates reported in Goodman (2000) failed to reflect realistic estimates of the cesium-137 inventories directly below the tanks. (This was one of the conclusions discussed in the MSU report [Goodman 2000] and was one of the technical justifications for drilling the SX-108 slant borehole.)

	Estimated Tank S-104 Inventory Loss	Estimated Tank SX-107 Inventory Loss	Estimated Tank SX-108 Inventory Loss	Estimated Tank SX-109 Inventory Loss	Estimated Tank SX-113 Inventory Loss	Estimated Tank SX-115 Inventory Loss
Leak Volume	24,000 gal^a	6,350 gal^b	15,200 gal^b	989 gal^b	15,000 gal^a	50,000 gal^a
Chemicals	(kg)	(kg)	(kg)	(kg)	(kg)	(kg)
Sodium	1.82E+04	9.90E+03	2.37E+04	1.54E+03	1.05E+04	1.57E+04
Aluminum	3.83E+03	2.00E+03	4.78E+03	3.11E+02	1.95E+03	4.24E+03
Chromium	7.81E+02	4.71E+02	1.13E+03	7.33E+01	5.08E+02	5.03E+02
Nitrate	1.70E+04	7.40E+03	1.77E+04	1.15E+03	9.96E+03	3.87E+03
Nitrite	6.87E+03	4.49E+03	1.07E+04	6.99E+02	3.50E+03	9.23E+03
Radionuclides	(Ci)	(Ci)	(Ci)	(Ci)	(Ci)	(Ci)
Technetium-99	3.87E+00	5.03E+00	1.21E+01	7.84E-01	2.50E+00	5.52E+00
Cesium-137	1.14E+04	1.71E+04	4.10E+04	2.67E+03	7.34E+03	1.88E+04

^aLeak volumes from Hanlon (2001).

^bLeak volumes estimated from MSU kriging analysis of gamma logging data (see Jones et al. 2000a).

Inventory and leak volume estimates developed in Jones et al. (2000a) are listed in Table 3.4 and Appendix C, Section C.3.0. These estimates remain as reasonable estimates for use in leak impact assessment studies (Appendix E, Attachment E1). The HGL kriging analysis was more robust than the MSU efforts because only experimentally determined measurements were used by HGL, and correlation lengths determined by HGL were based on a single tank (i.e., tank SX-108). This was done because extensive data are available for tank SX-108; results based on tank **SX-108** were then applied to other **SX** farm tanks.

If the HGL kriging results had been used in developing the inventory estimates, the values for tanks **SX-108** and **SX-109** listed in Table 3.4 would have changed very little. However, the tank **SX-107** inventory estimates would have been slightly higher than those reported for tank **SX-108** in Table 3.4. Leak inventory estimates for tanks **S-104**, **SX-113**, and **SX-115** were based on historical leak volumes. Leak volumes from tanks **SX-113** and **SX-115** are well documented (Hanson et al. 1962; Raymond and Shdo 1966) whereas the leak volume from tank **S-104** is significantly more uncertain. The 24,000 gal (91,000 L) leak volume currently reported in *Waste Tank Summary Report for Month Ending March 31, 2001* (Hanlon 2001) for tank **S-104** is based on long-term liquid level decreases (Agnew et al. 1997). However, the waste footprint (see Appendix B, Section B.6.0) projected from field investigations using cone penetrometer techniques and spectral gamma logging data fail to document the inventory estimates shown in Table 3.4 for tank **S-104**. Thus, the tank **S-104** inventory estimates listed in Table 3.4 are conservative.

3.3.2 Speciation Analysis

Significant quantities of high-level waste (HLW) were lost to the soil column from large underground tanks in WMA S-SX during long-term storage of the wastes produced in the REDOX Plant. **An** understanding of the mechanisms of soil and waste reactions controlling the movement of tank waste through the vadose zone requires knowledge of waste components on a molecular level. However, this level of tank waste chemistry is generally not available because that level of understanding was not required for the original plant operations or for long-term storage and waste management. *REDOX Technical Manual* (GE 1951) and the updated flow sheets in *Standard Inventories of Chemicals and Radionuclides in Hanford Site Tank Wastes* (Kupfer et al. 1998) provide clear guidance **as** to the conditions required for successful separations process operations but only limited understanding of the underlying fundamental chemistry. Thus, the most practical approach for developing an understanding of the chemical species present in leaked tank waste comes from chemical equilibria-based computer models that develop speciation of bulk waste components. Chemical thermodynamic-based models of aqueous systems can predict reaction products if the controlling thermodynamic parameters are sufficiently well understood. However, the tank waste mixtures are extremely complex and many of the required thermodynamic parameters are only poorly understood. Because any thermodynamic-based modeling exercise involving a tank waste matrix will require many approximations and assumptions, speciation modeling results must be treated with considerable caution.

The preliminary scoping studies for REDOX waste speciation (Jones et al. 2000a) were conducted using the Environmental Simulation Program, a thermodynamic-based chemical process simulator that has been widely applied at the Hanford Site (MacLean and Eager 1998). As discussed in Section 3.3.1.1, the compositions of the wastes in SSTs at the time of suspected leaks were developed using the HDW model (Agnew 1997). The tank waste supernate compositions were then used as input to the Environmental Simulation Program model with the goal of developing a better understanding of chemical speciation of the wastes at the time of suspected leaks (Jones et al. 2000a). A separate S&T activity focusing on contaminant migration in the subsurface conducted speciation analysis of the leaked fluids from tanks SX-108 and SX-115 (Appendix D, Section D.7.3). The results reported in Appendix D, Section D.7.3 represent a far more detailed solution thermodynamic investigation than the results reported in Jones et al. (2000a). Appendix D, Section D.7.3 uses the Pitzer-based formulation for calculation activity coefficients, which is more consistent with contemporary geochemical modeling studies.

The historical records (Harmon 1949; GE 1951; Barney 1976) clearly show that it was well known that the solution chemistry of REDOX HLW was dominated by the aluminum ion solubility and the aluminum solubility was controlled by the free hydroxide ion concentration. Thus, much of the speciation modeling efforts focused on developing a better understanding of aluminum ion chemistry in the REDOX waste matrix. Such an understanding is potentially important in geochemical processes impacting tank waste movement in the subsurface.

The initial Environmental Simulation Program speciation modeling of REDOX HLW, reported in Jones et al. (2000a), assumed a 0.1 M free hydroxide concentration resulting in essentially all of the aluminum residing in the solid phase **as** aluminum hydroxide. However, in other

calculations (see Appendix C) the aluminum was shown to be primarily in the solution phase, as aluminate anion, at the likely free hydroxide concentrations in REDOX HLW. Much of the information in Appendix C, updating the preliminary speciation analysis reported in Jones et al. (2000a), was developed in response to questions raised in the Appendix D, Section D.7.3 speciation results. The initial step in any speciation modeling exercise is the development of a charge balance for the system. Jones et al. (2000a) fixes the hydroxide at 0.1 M and allows the sodium ion to vary until the overall charge balance is reached, leading to sodium ion concentration near 12 M. Appendix D, Section D.7.3 maintains the sodium ion concentration developed by the HDW model and allows hydroxide to be varied until a charge balance is reached. At equilibrium in tank SX-108 at 100 °C (212 °F), Appendix D, Section D.7.3 predicts the hydroxide to be 5.1 M and the pH to be 14.1 with essentially all of the aluminum to be in solution as aluminate anion. The Appendix D, Section D.7.3 speciation results are consistent with the conditions one would predict from process flow sheet data (GE 1951). Thus, the Appendix D, Section D.7.3 results are the preferred data set for geochemical modeling studies.

Corrections to errors in technetium-99 speciation estimates in Jones et al. (2000a) are also discussed briefly. The preliminary speciation modeling results suggesting that major fractions of the technetium-99 could reside in the solid phase as potassium pertechnetate (KTcO_4) in highly concentrated REDOX HLW (Jones et al. 2000a) are of considerable interest. Initial modeling runs indicated that the majority of technetium-99 in wastes in tank SX-108 was incorporated into the solid phase as potassium pertechnetate but in the more dilute tank SX-115 wastes the technetium-99 remained in the solution phase (Jones et al. 2000a). A detailed review of the supporting information reported along with the speciation modeling results indicated that the potassium pertechnetate solubility was being driven by an unrealistically large activity coefficient term. Resolution of this issue was referred back to OLI Systems,¹ the software vendor, for resolution. The vendor reported that a programming error was found in the code. Basically, the silicate ion activity was being summed with pertechnetate activity leading to errors in solubility estimates. After correcting this programming error, the model predicted that all technetium-99 remained in the solution phase in the tank waste composition in each SX farm tank. Although, to date, no technetium-99 analysis data have been found for REDOX HLW, the suggestion that technetium-99 tends to remain in the solution phase is consistent with experimental data for plutonium-uranium extraction HLW (Godfrey 1971).

3.3.3 Summary of Tank Leak Inventory Investigations

The Jones et al. (2000a) preliminary tank leak volume estimates, waste composition estimates, and inventory estimates of tank waste lost to the soil column in WMA S-SX remain as a reasonable data set for tank leak impact investigations. These data are summarized in Table 3.4. Speciation data reported in Appendix D, Section D.7.3 is the preferred source for geochemical modeling studies. Uncertainties remain about inventory estimates for leaks from tanks S-104 and SX-107. Because of these uncertainties, no modifications were made to the leak inventory

¹ OLI Systems, Inc., Morris Plains, New Jersey.

estimates published in Jones et al. (2000a). Any resolution of these uncertainties will require additional field characterization data.

3.3.4 Correlation Between Projected Inventory Estimates and Field Investigation Data

Soil sample analyses from the three boreholes drilled in the **SX tank farm** (41-09-39, SX-108 slant, and 299-W23-19) near tank leaks provide data that qualitatively validate the reliability of these inventory estimates. The analyses revealed the presence of several constituents (radionuclide and chemical) that either were not derived from natural sources or were naturally occurring but at concentration levels too large to be derived solely from natural sources. These findings clearly demonstrate the existence of a nearby non-natural source, with tank leak fluids being the leading candidate.

In the soils from the two boreholes (borehole 41-09-39 and the SX-108 slant borehole) considered to be contaminated primarily by the tank SX-108 leak, elevated concentrations of cesium-137, technetium-99, nitrate, nitrite, chloride, sulfate, sodium, and chromium are found that originated in the tank SX-108 leak fluid (Appendix B, Sections B.2.0 and B.4.0). These elements are among the more concentrated constituents projected by inventory estimates (Table 3.2 and Appendix C, Tables C.1 and C.2). Higher levels of chloride and sulfate also may be attributed to the leak. Concentration ranges of these constituents in borehole soils are provided in Table 3.5. Similarly, for borehole 299-W23-19, soils are assumed to be contaminated by the tank SX-115 leak and high concentrations of technetium-99, nitrate, nitrite, sodium, chromium, chloride and sulfate are found (Table 3.5).

Table 3.5. Summary of Tank Leak Constituent Concentrations and Technetium-99 to Nitrate Ratios in the SX Tank Farm Characterization Boreholes

Borehole		41-09-39	SX-108 Slant	299-W23-19
Constituents	Technetium-99 (pCi/L)	3.9E+05 to 1.2E+07	1.65E+07 to 2.37E+08	9.50E+04 to 3.3E+06
	Cesium-137 (pCi/g)	1.25E+05 to 1.76E+07	5.55E+05 to 9.57E+07	Negligible
	Sodium (mg/L)	1.02E+04 to 1.53E+04	6.53E+04 to 3.91E+05	4.78E+02 to 3.08E+03
	Chromium (mg/L)	1.75E+02 to 7.46E+02	5.02E+03 to 2.18E+04	3.22E+00 to 1.22E+02
	Nitrate (mg/L)	1.01E+05 to 4.16E+05	1.98E+05 to 9.94E+05	6.03E+03 to 2.60E+04
	Chloride (mg/L)	3.58E+02 to 4.21E+03	1.38E+03 to 6.71E+03	1.06E+02 to 2.15E+02
	Sulfate (mg/L)	5.79E+02 to 4.58E+03	1.93E+03 to 2.41E+04	1.72E+02 to 9.35E+02
Tc-99/ Nitrate (pCi/mg)		2.61E+01 to 4.44E+02	3.46E+00 to 4.77E+02	4.09E+01 to 3.15E+02
Tc-99/Nitrate (pCi/mg)*		1.72E+02	2.44E+02	1.13E+02

*The technetium-99/ nitrate ratios are the average of individual ratios by depth in the elevated concentration zones.

A comparison of relative concentrations of these constituents with estimates of relative concentrations in the tank fluid provides another indicator of tank leak fluids as the contaminant

source. This approach is limited because most constituents are distributed differently in the vadose zone as different chemical reactions exist for the constituents, resulting in variable retardation and migration of each constituent. Thus, the comparison is usually difficult to make. The most straightforward comparison is to consider the **technetium-99/nitrate** ratios in soil versus the **technetium-99/nitrate** plus nitrite ratios in the inventory estimates. Data and chemical speciation knowledge indicate that technetium-99 and nitrate are essentially nonreactive with soils and migrate together. The soil data indicate that nitrite reacts by oxidizing to nitrate, but migration rates are not affected by this process. Therefore, if the **technetium-99/nitrate** plus nitrite source is the tank SX-108 fluid and no other sources provide contaminants at the borehole location, the ratios should be consistent. Similarly, if the **technetium-99/nitrate** plus nitrite source for borehole 299-W23-19 contamination is the tank SX-115 fluid, the ratios between estimated tank fluid inventory values and measured soil values should be comparable.

The zones of elevated technetium-99 and nitrate concentrations in each borehole agree very closely with depth. The average of individual soil sample **technetium-99/nitrate** ratios by depth in the elevated concentration zones are listed in Table 3.5 for all three boreholes. The **technetium-99/nitrate** ratios calculated from technetium-99 and the sum of nitrate plus nitrite inventory estimates in Table 3.4 are 4.3×10^2 pCi/mg for the tank SX-108 leak fluid and 4.2×10^2 pCi/mg for the tank SX-115 leak fluid. These ratios are within factors of two to four of the measured ratios. This is a very close correlation given the natural heterogeneities of fluid migration in the vadose zone. This correlation strongly supports both the causal relationship between tank leaks and soil contamination and increases confidence in the inventory estimate based on historical record.

Other soil and soil-water characteristics that are significant relative to the projected leak inventories are the occurrences of elevated pH in soil column soils at the top of the contaminated zones and the absence of elevated aluminum and strontium-90 concentrations in soil water extracts. In all three boreholes, elevated pH values (greater than 8.5) occur at shallow depths in the Hanford formation subunit H1 and then decrease with depth to values approaching those normal to undisturbed vadose zone soil water (approximately 7.5 to 8). This pattern is consistent with an initial interaction between high pH tank leak solutions (estimated at greater than 12, Appendix D, Section D.7.3) at a depth when tank solution first comes into contact with the borehole soil water followed by longer interaction as tank solutions drain from the initial location and migrate vertically with pH-buffering reactions continuing to lower tank solution pH. The lack of aluminum in these soil samples is consistent with the speciation work (see Section 3.3.2 and Appendix D, Section D.7.3) suggesting that high dissolved aluminum concentrations require very high solution pH. If so, only a small decrease in pH such as would be expected shortly after tank fluid contact with the vadose zone soils would cause immediate formation of aluminum-bearing precipitates very near the leak location. The analyzed soil samples are presumably too far from the source to contain precipitated aluminum.

An unequivocal explanation for the lack of strontium-90 in soil samples cannot be provided. Either strontium-90 was not present in solution as predicted or it sorbed rapidly and fell out of solution near the leak location. If so, as with aluminum, the soil samples would be too far from the source to contain sorbed strontium-90.

3.3.5 Integration of Inventory Information for Risk-Producing Contaminants of Concern

In the previous section, a summary of data and inventory estimates is provided for the primary constituents determined to exist in tank leak fluids. Of these, technetium-99 and nitrate are highly mobile in the hydrogeologic environment and may contaminate groundwater at sufficient concentration levels to be of concern. Additional mobile constituents are estimated to be present in tank fluids at smaller concentrations that also must be considered as potential contributors to future environmental contamination (see the modeling and risk analysis discussion in Section 4.0). Given the tank leak inventory estimates, additional mobile radionuclide constituents include carbon-14, selenium-79, iodine-129, and the long-lived uranium isotopes (principally uranium-238 and uranium-234). Hazardous mobile constituents include chromium, fluoride, mercury, nitrate, nitrite, total uranium, and EDTA. Because estimates of human health risk levels provided by each of these constituents are generally proportional to its abundance in the vadose zone, vadose zone inventory estimates must be evaluated thoroughly, using all available information. The combination of both historical estimating approaches and data for contaminated soils provides a complementary and useful basis for completing this evaluation.

All of the identified constituents are listed in the tank leak inventory estimates (Appendix C). Technetium-99, nitrate, nitrite, and chromium are primary constituents and, except for nitrite, have all been detected in the SX tank farm exploratory boreholes at high enough concentrations over large enough depth intervals to clearly indicate a tank leak source. Nitrite is currently at relatively low levels in the vadose zone because it has largely oxidized to nitrate since initial discharge. If these constituents are largely mobile in soils, then their relative concentrations present at the time of leakage should be preserved in the contaminated regions of the vadose zone. Comparison of water extract concentrations with tank inventory estimates of these constituents shows remarkable consistency in relative concentrations between the constituents. This observed consistency increases confidence that inventory estimates are reasonably close to real values. Consequently, these constituents have been incorporated into the risk analysis as legitimate potential contributors to future environmental contamination and risk.

A second set of constituents (carbon-14, selenium-79, mercury, fluoride, and EDTA) are estimated to be present in relatively small quantities in the leaked fluid. Carbon-14 is the more abundant radionuclide and is estimated to occur at concentrations about seven to eight times less than technetium-99. Selenium-79 is estimated to occur at concentrations about 40 times less than technetium-99. Mercury, fluoride, and EDTA are estimated to occur at concentrations more than four orders of magnitude less than nitrate. None of these chemical constituents has been detected in vadose zone soil analyses. Attempts were made to measure mercury and selenium-79, but detection levels were too high to allow a positive measurement. Fluoride was measured but soil concentration values were indistinguishable from natural background. Carbon-14 and EDTA were not measured. For the purposes of modeling and risk calculations, inventory estimates were used as the basis for quantifying vadose zone inventory.

The final two constituents, iodine-129 and uranium isotopes, were measured in a small fraction of samples. Iodine-129 is found only in the SX-108 slant borehole at depths between 24 and 40 m (80 and 130 ft) bgs (Appendix B, Section B.4.0 and Appendix D, Section D.6.1). These soil samples also contain high technetium-99 concentrations. In these soil samples, technetium-99 to iodine-129 activity ratios exceed 2,000. This compares to an estimated

technetium-99 to iodine-129 activity ratio of about 530 assumed for tank SX-108 supernate and supernate in the other assumed leaking tanks in WMA S-SX. Assuming that technetium-99 and iodine-129 are similarly distributed in the vadose zone because of their chemically similar behavior, this is a valid and reasonably close comparison. It is not surprising that the field ratios are lower given that estimates of iodine-129 content in tank fluids ignore the possibility that some portion of iodine-129 volatilizes during fuel processing and never reaches the tanks. For purposes of risk estimates, the estimated supernate iodine content provides a reasonable and conservative source term estimate.

Uranium measurements in vadose zone soils are complicated by the fact that naturally occurring uranium is ubiquitous in vadose zone soils and when measured concentrations are close to natural concentration levels, determination of additional sources is uncertain. In these studies, uranium was analyzed from extracts of water and acid contacted with borehole soils. The largest water extract concentrations (7 to 55 $\mu\text{g/L}$) occurred in the tank SX-115 borehole, 299-W23-19, between 22 and 38 m (73 and 126 ft) bgs. This range slightly exceeds water extract values typical for uncontaminated soils (e.g., about 1 to 10 $\mu\text{g/L}$ are measured in water extracts from 299-W22-48 and 299-W22-50, two RCRA boreholes east of the SX tank farm; sitewide background levels range from 0.5 to 13.9 $\mu\text{g/L}$ [DOE-RL 1997a]). Only two samples in the SX-108 slant borehole show elevated uranium water extract concentrations (140 and 210 $\mu\text{g/L}$). No samples from borehole 41-09-39 yield water extract uranium values above the natural range.

It is unclear from the water extract data whether the slight elevations in dissolved uranium from these soil samples represent contributions from tank leak sources. To get another perspective on this, it is instructive to compare the uranium to chromium concentration ratios in borehole 299-W23-19 versus the estimated inventory values for the leaked tank SX-115 borehole. This comparison is indicated by the coincidence of highest uranium and chromium water extract values over the same depth interval in the borehole. Although chromium shows slightly retarded migration in these soils it is still a very mobile constituent and could be a surrogate for uranium in the risk analysis. The average uranium to chromium water extract values by mass is about 0.0015. For the tank SX-115 fluid, the estimated uranium to chromium inventory ratio is about 7, a significant discrepancy of about 3 orders of magnitude. Two explanations are feasible. First, the uranium inventory estimate may be excessively high. Historical records indicate that the uranium would have been in the sludge fraction in the high-hydroxide REDOX wastes (Anderson 1954). Alternately, uranium may be present at high values in the leaking tank fluid, but is not mobile in the soil environment such that the bulk of the uranium is fixed in the soil closer to the tank leak source. In either case, an assumption of a large and mobile uranium inventory as a vadose zone source term for risk calculations is not warranted. Given the proportionality between risk estimates and starting inventory, use of a small uranium inventory indicated by the measured uranium to chromium ratio will result in an insignificant risk estimate compared to the other constituents. In the risk analysis (Section 4.0), uranium has not been included as a risk-producing contributor because of the inventory/risk relationship coupled with uncertainty about the real presence of tank source uranium in the vadose zone.

3.4 CONCEPTUAL MODEL DESCRIPTION

An initial conceptualization of contaminant occurrences and characteristics in WMA S-SX was developed to support a work plan for additional characterization (Johnson et al. 1999).

The additional database (referred to in this section as new work or new data) that has been developed has provided support for and clarification of the initial conceptual models. The focus of the conceptual models has been those events and processes that have led to the current state of vadose zone and near-field unconfined aquifer contamination. In this section, a description of the conceptual models is provided in which the new data provided in this WMA S-SX FIR are correlated with the appropriate aspects of the conceptualization. As before, it is most convenient to organize conceptualization by primary areas of contamination. These include the areas around tanks SX-107, SX-108, SX-109; tank SX-115, and tank S-104.

3.4.1 Conceptual Model for the Contamination Area Below Tanks SX-107, SX-108, and SX-109

Recent activities and data relevant to vadose zone contamination in this area include the following:

- Deepening of borehole 41-09-39 and soil samples characterization from 40 m (130 ft) bgs to groundwater; additional characterization of selected soil samples between 8 and 40 m (25 and 130 ft) bgs (see Appendix B, Section B.2.0)
- Drilling of a slant borehole beneath tank SX-108, soil sample characterization from 17 to 41 m (55 to 135 ft) bgs, and gamma moisture logging with depth
- Additional calculations to estimate tank supernate inventory and speciation chemistry (Appendix C, Sections C.3.4 and C.3.5)
- Kriging estimates of cesium-137 inventory by MSU and HGL (Appendix C, Section C.3.3)
- Modeling of thermal effects on vadose zone moisture and temperature history and contaminant transport in the vadose zone from 1955 to present (Appendix D, Sections D.7.1, D.7.2 and D.7.4).

These data combined with existing data from historical and spectral gamma logging, historical records, limited early soil and tank supernate analyses (Raymond and Shdo 1966), groundwater sample analyses, and hydrogeologic data, provide the basis for the conceptual model.

The vadose zone contamination in this region is dominated by the waste leaked from tank SX-108 between 1962 and 1967. Smaller-volume leaks occurred from tanks SX-107 and SX-109. The vadose zone contamination is primarily derived from the tank SX-108 leak and is the focus of this conceptual model.

Additional studies have been completed to estimate vadose zone contamination derived from these tank leaks (Section 3.4 and Appendix C). Collection of new data has focused on statistical manipulation of cesium-137 spectral gamma data to estimate more directly the total inventory

and inventory distribution in the vadose zone (i.e., kriging methods). Estimates of other contaminants of interest are then determined by ratio to cesium-137 inventory in the tank supernate using the HDW model as the basis for estimate. Conversely, earlier inventory estimates (Johnson et al. 1999) were derived using leak volume estimates as the starting point, combined with supernate concentration estimates. The tank SX-108 leak estimates ranging from 9,100 to 770,000 L (2,400 to 203,000 gal) were noted with a similar range in contaminant inventory estimates. The updated database provides a smaller range of vadose zone inventory estimates. These estimates are more consistent with volumes estimated by the historical record.

As in the previous conceptualization, the new database supports the idea of a two-phase process leading to the current state of contamination. The two phases are distinguished by different conditions and mechanisms controlling contaminant migration. In the first phase, one or more rapid releases of tank supernate into the vadose zone occurred, creating a hydraulic driver that superseded natural infiltration. Both vertical and horizontal migration occurred quickly. Elevated temperatures occurred in much of the local vadose zone created by radioactive constituents present inside the tanks and in the leaked tank waste. Temperatures exceeded boiling near tanks SX-107, SX-108, and SX-109, which dried soils and inhibited recharge.

The primary indicator of tank fluid migration in the initial phase is cesium-137 distribution and more indirectly pH measured in soil samples from boreholes 41-09-39 to the west of tank SX-108 and the SX-108 slant borehole. Normally, cesium-137 sorbs near the leak and drops out of solution very quickly; however, in this instance the supernate chemistry controlled the local chemical environment. Historical knowledge of tank supernate chemistry and laboratory sorption work (see Appendix D, Section D.3.0) indicates that the appropriate conditions to create high cesium-137 mobility did exist at the time of tank leak. The primary enabling conditions are a combination of very high sodium and cesium-137 concentrations in tank fluid. Under these conditions, sodium competes successfully with cesium-137 for sorption sites, forcing cesium-137 to remain in solution.

High cesium-137 concentrations (more than 5×10^5 pCi/g) in the SX-108 slant borehole (Figure 3.8) begin at 17 m (55 ft) bgs in Hanford formation subunit H1a and continue throughout subunits H1 and H2 between 17 and 27 m (55 and 89 ft) bgs. This is a substantially thicker high-concentration zone than that observed in borehole 41-09-39 where similar concentrations occur between 19 and 25 m (61 and 83 ft) bgs, primarily in subunit H1. This distribution suggests that vertical migration was more significant near the leak origin, although maximum depth of cesium-137 migration is not greatly different in the two boreholes. Conversely, the borehole 41-09-39 data indicate extensive horizontal movement away from the tank that was largely confined to subunit H1, a coarse sand-gravel unit that lies near the tank bottom and dips gently to the southwest (Figure 3.3). This correlation indicates that the hydrologic properties of subunit H1 combined with the high-rate, high-volume tank leak caused extensive horizontal migration. Figure 3.7 illustrates this horizontally biased migration pattern generated by kriging analysis of site-specific spectral gamma data.

Figure 3.8. Cesium-137 in Vadose Sediments at the SX-108 Slant Borehole

Additional features of cesium-137 distribution in these boreholes include separate high-concentration zones or, within the primary high concentration zones, smaller zones of high and low concentrations. For example, in borehole 41-09-39, in addition to the primary high-concentration zone in subunit H1, a secondary peak concentration also occurs in subunit H2 at 31 and 33 m (103 and 109 ft) bgs. This multiple peak characteristic is seen frequently with other tank fluid contaminants as well in these soil columns. These variations could be attributed to variability in hydrologic properties for soil lenses occurring at different depths, geochemical variability affecting contaminant migration, or multiple leak events. The two-leak concept is supported by iodine fission product isotope measurements (iodine-127/iodine-129) in the SX-108 slant borehole (Appendix D, Section D.6.1) showing two distinct isotopic ratio signatures separated by depth in the analyzed soils. The two-leak concept adds complexity to the genesis of current vadose zone contamination from tank leaks but does not significantly alter the proposed conceptualization of contaminant migration.

Thermal-effects modeling results suggest at least two mechanisms that also may have influenced contaminant migration during the initial phase. First, temperatures exceeded 100°C (212 °F) in soils near the tanks, creating dry zones that may have extended to and below subunit H1 for some time. If so, tank fluid would have boiled off, leaving contaminants in place until temperatures dropped below boiling and allowed re-saturation and a resumption of recharge. Second, a heat-pipe effect may have occurred near the 100 °C (212 °F) isotherm with water vapor being driven away from the heat source until it reached a cooler region and condensed and liquid water being drawn toward the heat source by capillary pressure. Constituents in the water vapor and water being pulled back toward the heat source would tend to concentrate near the point of vaporization. Whether or not this chemical concentration process could have affected tank fluid constituents is not known. The net effect would have been to delay further migration of contaminants by maintaining dry conditions where tank fluid contaminants were initially deposited and preventing recharge until temperatures dropped below 100°C (212 °F).

The second phase of tank fluid migration began when the leak stopped, reducing and finally eliminating the hydraulic driver for relatively rapid vertical and lateral migration of the tank fluid. Over time, vadose zone soil temperatures dropped below boiling and the physical driver became infiltration from natural events with vertical and lateral migration essentially governed by natural recharge and geologic heterogeneities. The lateral migration is induced by heterogeneities and moisture-dependent anisotropy (Section 3.1.2 and Appendix E). Also, control of local chemical conditions by tank fluid chemistry diminished as tank fluids migrated downward and reacted with the ambient soil phases and pore water. During this time, a complex series of transient conditions evolved, affecting contaminant behavior and other chemical parameters.

The second phase of migration is indicated by the occurrence of tank fluid contaminants other than cesium-137 at different depths in the vadose zone in these boreholes. With downward movement and changing chemical conditions, the more mobile tank fluid constituents migrated deeper in the vadose zone, creating a crude chromatographic profile, an observation common to both boreholes. These data provide examples of a presumably more widespread occurrence over the area marked by cesium-137 distribution attributed to this leak. However, additional data are not available to evaluate the radial lateral or three-dimensional aspects of second-phase migration.

The constituents present at maximum concentrations deepest in the boreholes are nitrate and technetium-99, whose relative concentration profiles with depth are nearly identical. Maximum depths of these high concentration zones in both boreholes are similar but they occur somewhat deeper in the stratigraphic sequence under tank SX-108 (e.g., maximum nitrate and technetium-99 concentrations occur in subunit H2 and into Plio-Pleistocene subunit PPIz versus maximum concentrations in subunit H2 in borehole 41-09-39). Their characteristics are as follows.

- In the SX-108 slant borehole, elevated nitrate concentrations are measured throughout the borehole (17 to 44 m [55 to 145 ft] bgs) with maximum values of 180,000 to 995,000 mg/L measured between 25 and 39 m [81 and 130 ft] bgs (Figure 3.9). In borehole 41-09-39, elevated nitrate concentrations are measured between 20 and 41 m (65 and 136 ft) bgs, with maximum values of 101,000 to 417,000 mg/L between 25 and 39 m (83 and 127 ft) bgs (Figure 3.10).
- In the SX-108 slant borehole, technetium-99 occurs at elevated concentrations throughout the borehole with maximum values of about 1.6×10^7 to 2.4×10^8 pCi/L between 26 and 42 m (85 and 138 ft) bgs (Figure 3.11). In borehole 41-09-39, elevated technetium-99 concentrations are measured between 17 and 39 m (56 and 127 ft) bgs with maximum values of 3.9×10^5 to 1.2×10^8 pCi/L between 25 and 39 m (83 and 127 ft) bgs (Figure 3.12).

The depths of high concentration ranges of these constituents compared to cesium-137 clearly show greater vertical migration over time of the mobile constituents as expected. Interestingly, the amount of separation between the centers of mass of cesium-137 versus nitrate and technetium-99 are similar in both boreholes. Assuming the separation length is a qualitative indicator of second-phase migration, recharge conditions are relatively similar in both boreholes.

Tank waste constituents showing intermediate retardation between cesium-137 and nitrate/technetium-99 are sodium and chromium. The high concentration zones occur at a lower depth relative to cesium-137 zones and at a higher depth relative to nitrate/technetium-99 zones. Their characteristics include the following.

- In the SX-108 slant borehole, maximum sodium concentrations begin abruptly at 25 m (81 ft) bgs, remain elevated between 65,000 and 391,000 mg/L through 40 m (130 ft) bgs except at 32 m (105.6 ft) bgs where sodium concentration **drops** to 691 mg/L (Figure 3.13). In borehole 41-09-39, maximum sodium concentrations begin abruptly at 25 m (81 ft) bgs and remain elevated between 10,000 and 15,000 mg/L through 34 m (112 ft) bgs (Figure 3.14).
- Chromium concentration values in the SX-108 slant borehole increase above background beginning at 20 m (68 ft) bgs and show maximum values between 5,000 and 22,000 mg/L from 25 to 40 m (81 to 130 ft) bgs (Figure 3.11). The peak concentration of more than 22,000 mg/L occurs at 30 m (97 ft) bgs. In borehole 41-09-39, chromium concentration values increase above background beginning at 20 m (66 ft) bgs and reach maximum concentrations between 175 and 750 mg/L between 25 and 34 m (81 and 112 ft) bgs.

Figure 3.9. Anions Calculated and Actual Porewaters
for SX-108 Slant Borehole Sediments

Figure 3.10. Concentrations of pH, Electrical Conductivity, and Nitrate in Dilution-Corrected Water Extract

Figure 3.11. Trace Metals Calculated and Actual Porewaters
for SX-108 Slant Borehole Sediments

Figure 3.12. Technetium-99 Activity in Porewater in Borehole 41-09-39

Figure 3.13. Cations Calculated and Actual Porewaters for SX-108 Slant Borehole Sediments

Sodium retardation is attributed to successful competition with divalent cations (cesium-137, calcium, magnesium, and natural strontium) and partial sorption on soil minerals. This hypothesis is supported by depletion of these cations in the high sodium zones and increased concentrations just deeper than the sodium front in both boreholes. The loss of cesium-137 mobility is attributed to the separation of high sodium concentrations from cesium-137 as downward migration of tank fluid occurs carrying excess sodium away. Chromium retardation is attributed to partial reduction by naturally occurring iron(II) in soil minerals.

Both phases of the tank fluid migration history appear to be represented by the changes in pH values with depth measured in borehole 41-09-39 (Figure 3.10) and the SX-108 (Figure 3.15) slant borehole soils. Tank supernate pH was initially much higher than soil water pH (e.g., over 10 for tank supernate, and 7.5 to 8 for soil water). As the tank supernate interactions with soil phases and soil water progress, intermediate pH values should occur and ultimately approach soil water values as the buffering capacity present in the soil column eventually prevails. Assuming that increasing reaction occurs at increasing depth over time, pH values should drop with depth. This behavior is evident in borehole 41-09-39 where pH values are greatest (over 8.7) in Hanford formation subunit H1 coincident with the highest concentration of cesium-137 in the borehole and decrease to about 8 in subunit H2 where the mobile constituents are concentrated.

The fact that the leading edge of the tank fluid plume stops at the Plio-Pleistocene unit in these boreholes creates ambiguity about the direction of recent tank fluid migration and the prediction of future migration. The Plio-Pleistocene unit is a thick, low-permeability unit in this area and could provide a significant retardation to downward moisture movement. As suggested by data in Serne et al. (2001c, 2001d), tank leak fluid may have progressed only to the Plio-Pleistocene unit or may have reached the Plio-Pleistocene unit and been dispersed laterally. Simple calculations assuming enhanced natural recharge rates of 10 cm/yr (4 in./yr) allowed by tank farm gravel covers show that tank fluids could have been driven deeper than the Plio-Pleistocene unit (Serne et al. 2001b). Because tank waste constituents were not encountered below the Plio-Pleistocene unit, the conclusion could be that some lateral migration has also occurred. However, quantification of the effective recharge rate remains uncertain. As discussed in Section 3.1.2, no site-specific recharge estimates are available for tank farm conditions. In the absence of site-specific data, estimates are based on long-term lysimeter experiments that mimic the non-vegetated, gravelly conditions at the tank farms.

In addition to the potential for the Plio-Pleistocene unit acting as a partially effective barrier to vertical flow, soil column heating from radioactive constituents in tank waste and tank leaks may have had a significant impact on recharge, particularly early during tank farm operations when radioactive decay was at a maximum. The thermal modeling results indicate a rather lengthy drying region around the leaks (several decades), a process that could have slowed or prevented local recharge for sometime.

3.4.2 Conceptual Model of the Tank SX-115 Area Contamination

New activities and data relevant to vadose zone contamination in this area include the following:

- Drilling of vertical borehole 299-W23-19 near the southwest part of tank SX-115, soil sample characterization from 10 to 62 m (32 to 205 ft) bgs, and gamma/moisture logging with depth
- Ongoing collection of groundwater contamination data from groundwater monitoring wells at the south end of the SX tank farm.

These data, combined with existing data from historical and spectral gamma logging, historical records, limited early soil and tank supernate analyses (Raymond and Shdo 1966), and hydrogeologic data, provide the basis for the conceptual model.

The vadose zone contamination in this region is dominated by the leak or leaks from tank SX-115 (190,000 L [50,000 gal] in 1965) and is the focus of the conceptual model. Given the similarity of the leak event and the stratigraphy with the tank SX-108 leak event, a two-stage contaminant migration process is proposed. Unlike the tank SX-108 contamination area where current cesium-137 distribution is postulated to indicate the movement of tank fluid immediately after leakage, no similar indicator is present in the tank SX-115 area. Tank SX-115 supernate chemistry clearly did not enhance cesium-137 mobility causing rapid sorption onto soils very close to the leak location. New data from borehole 299-W23-19 provides little indication of early migration except perhaps for a small zone of elevated pH in subunit H1a that may mark the remnants of early high pH tank fluid with moderately alkaline porewater. No other borehole data are available to provide an indication of horizontal distribution.

Whether or not significant early lateral migration occurred in the vadose zone shortly after initiation of the tank SX-115 leak, subsequent downward movement in the second phase of migration would have had to have been extensive and spatially complex if the presence of high technetium-99 concentrations at the new monitoring well 299-W23-19 is assumed to be derived from the tank SX-115 leak. Specific soils and groundwater sample data from this borehole that support this hypothesis include the following.

- Elevated pH and chromium levels (Figures 3.16 and 3.17, respectively) indicate the depth at which tank fluids first interact with soil, at about 22 m (73 ft), in subunit H1a and within 1.5 m (5 ft) of the subunits H1a/H1 contact. A distinctive maximum pH value zone (pH greater than 9) exists in subunit H1 at 23 to 26 m (75 to 86 ft) bgs. At lower depths, pH values range from 8 to 8.5.
- Tank fluid contamination in this borehole is marked by maximum concentrations of mobile constituents in the Plio-Pleistocene unit (Figures 3.17 and 3.18), including technetium-99 (at 37 to 46 m [123 to 150 ft] bgs), nitrate and chloride (at 38 to 46 m [126 to 150 ft] bgs). Also, slightly elevated technetium-99 concentrations extend from the Plio-Pleistocene unit to the water table in this borehole.
- Technetium-99/nitrate ratios in soil water extracts from the high concentration intervals in the vadose zone are essentially the same as that in the borehole groundwater samples.

Figure 3.16. Calculated and Actual Porewater pH and Electrical Conductivity Values for Borehole 299-W23-19 Sediments

Figure 3.17. Trace Metals Calculated from Sediment Water Extracts and Actual Porewaters for 299-W23-19 Sediment

Figure 3.18. Anions Calculated and Actual Porewaters
for Borehole 299-W23-19 Sediments

- Soil moisture contents in soils are elevated above undisturbed soil conditions and matric potential measurements indicate drainage.
- Groundwater monitoring data show elevated technetium-99, chromium and nitrate concentrations in a series of wells covering a narrow east-west zone in the unconfined aquifer along the south boundary of the SX tank farm. The maximum technetium-99 concentrations occurred in borehole 299-W23-19 (81,500 pCi/L in March 2001) and are interpreted to be close to the point of contaminant entry into the vadose zone. The technetium-99/nitrate ratios (0.11 pCi/μg) at this borehole are present in boreholes 299-W22-46 and 299-W22-50 (Figure 3.19).

A comparison of current and historical conditions in the tanks SX-107, SX-108, and SX-109 leak area versus the tank SX-115 leak area also suggests accelerated migration of tank SX-115 waste. The tanks SX-107, SX-108, and SX-109 area shares a similar vadose zone stratigraphy with the tank SX-115 area, but is characterized by a drier soil column (e.g., soil moisture content in boreholes 41-09-39 and the SX-108 slant borehole versus borehole 299-W23-19) and the absence of both associated groundwater contamination and known anthropomorphic leakage or leak sources. Tank fluid mobile constituents technetium and nitrate in borehole 299-W23-19 are concentrated at lower depths compared to borehole 41-09-39 and the SX-108 slant borehole (e.g., maximum vadose zone concentrations in the Plio-Pleistocene unit versus the H2 subunit).

Collectively, these data support a hypothesis that contaminant migration in the tank SX-115 area of the vadose zone occurred rapidly in both the horizontal and vertical direction in the vadose zone and broke through to the unconfined aquifer somewhere upgradient (west) of borehole 299-W23-19. Circumstantial evidence of recent extensive waterline leaks near tank SX-115 could have provided the needed source of water that would explain the rapid contaminant migration rates and high concentrations for technetium-99, chromium, and nitrate in groundwater at borehole 299-W23-19. The minimum amount of contamination in the borehole 299-W23-19 soil column between the Plio-Pleistocene unit and the water table indicates that breakthrough did not occur at this borehole and that some lateral movement of tank fluid contaminants in the vadose zone is necessary if the groundwater contamination source is the tank SX-115 leak. Lateral movement may have occurred at one or more depths because of stratigraphic controls, one plausible unit being the Plio-Pleistocene unit, another being subunit H1. Both units predispose movement to the west, the general down-dip direction (Figure 3.3). This hypothesis also requires that a fairly extensive and multi-directional distribution in the vadose zone (e.g., tens of meters) of water from the water line leaks must have occurred to allow contact between water and contaminants and subsequent rapid migration. This mechanism is feasible because of the combination of stratigraphic controls promoting horizontal flow and high volume rapid fluid discharge into the vadose zone created by water line leak(s).

Figure 3.19. Technetium-99/Nitrate Ratios for Waste Management Area S-SX Network Wells

2001/DCL/S-SX/002

3.4.3 Conceptual Model of the Tank S-104 Area

Additional data that have been collected in the tank S-104 area are limited to the investigation of shallow soil contamination using a cone penetrometer and collection of groundwater monitoring samples downstream of the tank S-104 area. The cone penetrometer data provided minimal data relevant to the tank S-104 leak. The groundwater data consist of elevated levels of technetium-99 and nitrate, which are tentatively linked to the tank S-104 leak by relative location and historical knowledge. This suggests that the tank S-104 leak is the largest known plausible technetium-99 source in S tank farm. Technetium-99 concentrations at wells 299-W22-44 and 299-W22-48 currently appear to be going through a short-term spiking event in downstream wells at peak concentrations of the same order of magnitude as found at well 299-W22-46 attributed to the tank SX-115 leak. Also, technetium-99/nitrate ratios are elevated above background.

Given the limited amount of new data, the conceptual model of contamination genesis and migration remains unchanged. Environmental contamination indicators at this site resemble that of the tank SX-115 leak. First, vadose zone contamination began with a relatively large tank leak where highly reactive contaminants (e.g., cesium-137) dropped out of solution rapidly and mobile constituents continued to migrate with tank fluid. Second, at least one large pipe leak is known to have occurred in the region and the local topography has been conducive to collection of runoff and snowmelt. Accelerated recharge is plausible and mobile constituent contaminants (e.g., technetium-99) currently do appear in groundwater that may be attributed to this source. The timing of technetium-99 groundwater contamination that may be attributed to the tank S-104 leak is more or less concurrent with the technetium-99 groundwater contamination attributed to the tank SX-115 leak.

3.4.4 Representation of Conceptual Models in Contaminant Migration Modeling

Projection of future contaminant migration through modeling (see Section 4.0 and Appendix E) is necessary to make long-term waste management decisions where multi-generational environmental impact is a key concern of regulators and stakeholders. Frequently, as in the case of vadose zone Contamination, the evolution of contaminant distribution into the natural environment is a slow process that can take many decades or longer to evolve. When waste management decisions are required in a short timeframe, modeling is the only tool available to estimate potential human health risk estimates needed to make near-term decisions. Modeling approaches that provide useful results must accommodate the uncertainties intrinsic to both the natural system being modeled and estimates of future events and outcomes.

Natural system heterogeneities, including those inherent in the environmental setting and those associated with physical and chemical processes controlling contaminant migration, cannot be truly simulated in real time and space because of an insufficient database and limited computational capabilities. Therefore, simplifying assumptions and representations of real conditions and events that provide a reasonably conservative (e.g., bounding) approximation rather than a true prediction of future environmental impact and associated risk must be selected. At the same time, the degree of conservatism must be selected carefully to avoid very large risk estimates that require costly and inefficient waste management actions.

Given this perspective, aspects of the conceptual model that have been incorporated into the base case numerical modeling configuration include the following:

- Two-dimensional modeling of contaminant transport through the vadose zone in representative cross-sections at each of the three high-contamination areas
- Placement of initial vadose zone inventory in a present-day configuration consistent with historical knowledge and field data
- Imposition of several steady state recharge rates that approximate average yearly recharge from natural precipitation, depending on the surface barrier characteristics as the hydraulic driver for contaminant transport to the underlying aquifer.

Having taken this approach, aspects of the conceptual model have not been simulated or are only simulated by the primary numerical model summarized in Section 4.0. A deliberate decision was made not to model the initial leak events but to model future contaminant migration beginning with current conditions. This decision allowed avoidance of extremely complex events for which only a fraction of the necessary data is available. The leak events were highly transient involving variable release rates, nonisothermal conditions (spatial and temporal), and variable tank leak chemistry as tank fluids migrated through the soil column, interacting with soils and soil water. Some aspects of these events have been modeled by the S&T activity (Appendix D).

The potential drawback of this decision was the chance that processes actively influencing contaminant migration during the initial leakage phase could still be affecting contaminant mobility such that modeling results do not account for still active primary driving forces. Chief among these potentially significant processes include the following:

- Heat effects on fluid migration and contaminant chemical reactivity
- Tank fluid chemistry effects on contaminant mobility.

The evolution of thermal gradients has been modeled by the S&T activity (Appendix D). Results indicate that current and future profiles are reaching a quasi steady state condition that leaves ambient temperatures not greatly above natural condition values, a condition that should not seriously affect future moisture movement. Lingering heat effects on moisture would likely retard moisture movement relative to that assumed in the modeling analysis. Thus, an isothermal modeling approach should provide a conservative result (faster travel time and higher contamination levels in the unconfined aquifer) and is used (Section 4.0).

Empirical desorption tests on soils have been used from the characterization boreholes (Appendix B) to estimate current in situ mobility. In particular, continuation of initially very high cesium-137 mobility in the tank SX-108 leak needed to be assessed. The results indicate that the mobility of contaminants of interest are now relatively similar to those observed in undisturbed Hanford Site soils. In essence, tank fluid chemistry has been buffered to the extent that it no longer dominates contaminant behavior compared to undisturbed soil conditions. Assumptions of normal retardation coefficients are adequate to represent likely future occurrence of contaminants in the unconfined aquifer. Realistically, only technetium-99, nitrate, and chromium—the constituents currently observed in groundwater and attributed to tank leak sources—are likely to reach groundwater from this source at other than negligible concentration

levels. Iodine-129 may also be of some concern but has only been measured in a small zone at the bottom of the SX-108 slant borehole. These contaminants are assumed to be completely mobile ($K_d = 0$ mL/g) in the modeling analyses. This assumption maximizes aquifer concentration estimates and eliminates any relevance of geochemical conditions to the groundwater contamination estimate.

Heterogeneities in vadose zone hydrologic properties and recharge events are considered in the modeling analysis. Heterogeneities occur somewhat randomly over small regions that cannot be characterized. Geologic heterogeneities include stratigraphic controls that may induce lateral migration to occur. Clastic dike features may provide conduits for preferential flow. As noted above, particularly in the tank SX-115 area, the Plio-Pleistocene unit may have a variable capability to divert fluid migration. The modeling approach considers hydrologic properties and variable, moisture-dependent anisotropy for the major geologic strata in the vadose zone based on laboratory measurements of hydrologic properties for samples representative of each stratigraphic unit (Section 4.0 and Appendix E). Clastic dikes are known to occur in the vicinity of the WMA S-SX tank leaks and have been postulated as significant pathways for enhancing contaminant migration rates and groundwater concentrations. Because of this concern, a sensitivity case (Section 4.0) was considered to evaluate the influence of a clastic dike feature on contaminant migration, despite the fact that exact site-specific location and hydrologic properties of these features are not known.

Recharge events derived from natural processes (i.e., precipitation, snowmelt, and runoff) are transient, random events. Similarly, water-line leaks that are assumed to occur at various locations in WMA S-SX are unpredictable events. Neither of these types of processes are modeled in this analysis realistically. Recharge from precipitation and infiltration is modeled as a steady-state event that is correlated to a yearly average. This is a standard, well-accepted approach and quantification of recharge is based on lysimeter data of recharge through gravel materials that are similar to tank farm barriers. Events that have caused short-term, high volume water releases to the vadose zone (water-line leaks) are only evaluated in a few sensitivity cases for two reasons.

- The database that adequately quantifies water fluxes from these events does not exist and probably cannot be generated.
- The focus of the modeling analysis is long-term contaminant migration.

Steps already have been taken to eliminate the possibility of future high-volume discharge occurrences (e.g., underground water lines will be entirely capped off, surface covers will be engineered to minimize infiltration and prevent ponding of runoff or snowmelt) in FY 2001.

3.5 INTERIM MEASURES

The interim measures and ICMs that have been evaluated and/or implemented as they relate to WMA S-SX are described in this section. Interim measures are initial response actions that can be taken while characterization activities are underway and while long-term strategies are being developed to reduce the impacts of tank leaks on groundwater. Interim measures do not require comprehensive evaluation in a CMS. Interim measures identified to date for WMA S-SX focus

on actions to minimize infiltration and contaminant migration to groundwater. Four categories of interim measures have been implemented at WMA S-SX during the past three years (see Section 3.5.1).

ICMs are response actions with the objective of reducing contaminant migration to groundwater to acceptable regulatory levels and that require balancing risk, benefits, and costs. In general, ICMs involve a substantial commitment of resources, require a more thorough evaluation, and are intended to provide a more permanent solution to the long-term threats posed by a release. Detailed evaluation of the proposed WMA S-SX ICMs will be undertaken in a CMS or an accelerated CMS pending results of this FIR.

Detailed information on WMA S-SX interim measures and ICMs is contained in Appendix F.

3.5.1 Interim Measures Identification

An engineering report (FFS 1999) was published November 1999 that assessed potential measures to limit infiltration through the vadose zone at the SST farms. That report was updated and revised in May 2001 (Anderson 2001). Anderson (2001) evaluates leaking water lines, wells within the SST farms, and surface water (both recharge and run-on). Updated rough order of magnitude cost estimates are also provided in Anderson (2001).

Included in Anderson (2001) are a number of interim measures that are ‘good housekeeping’ actions considered for implementation because they clearly would reduce water infiltration at the tank farms and limit the migration of contamination through the vadose zone.

3.5.1.1 Abandonment of Active Water Lines. Combined, the S and SX tank farms contain approximately 1,930 m (6,300 ft) of active water lines that could be or have been abandoned to eliminate persistent leaks and prevent future water line breaks. These lines were mainly installed during original tank farm construction in the 1950s and 1960s and have exceeded their design life of 20 years. Pipe breaks, failed leaded joints, and poorly functioning gate valves are common. The Hanford Site-wide failure rate appears to be increasing geometrically. Four pressurized water lines entering the S and SX tank farms from the east were identified as still potentially operational or pressurized.

3.5.1.2 Decommissioning Unfit-for-Use Wells. Wells and drywells identified as unfit-for-use in Anderson (2001) are potential preferential pathways for downward contaminant migration. It is important to note that many of the wells and boreholes do not extend to the groundwater. Anderson (2001) identifies six wells in the S and SX tank farms that are potential Priority 1 candidates for near-term decommissioning.

3.5.1.3 Upgradient Surface Water Run-on Control Measures. Upgradient surface water run-on control consists of some combination of regraded ground surfaces, gravel berms, asphalt pavement, and concrete curbs and valley drains constructed outside the SST farms to prevent surface water from pressurized water-line leaks and unusual meteorological events from flowing onto the tank farm areas. Photographic evidence shows that low areas of the SX tank farm were flooded in 1979 when rapid snowmelt occurred. Anderson (2001) recommends that run-on control be established to prevent surface water from entering the SST farms from outside sources even if no other interim measures are selected to reduce infiltration within each SST.

3.5.2 Interim Corrective Measures Identification

ICMs have the same overall purpose as interim measures. Because of size, complexity, or impact to operations, a more careful study must be performed before an ICM is implemented. Many potential ICMs for mitigation of potential impacts at WMA S-SX have been identified; however, some of these potential ICMs are likely to be implemented sooner than others.

3.5.2.1 Identification of Potential Near-Term Interim Corrective Measures. The activities that have been undertaken to identify potential ICMs for all of the WMAs are as follows.

- In 1992 an engineering study, documented in *Single-Shell Tank Interim Cover Engineering Study* (Young et al. 1992), evaluating 4 approaches for reducing surface infiltration at all of the WMAs was completed. The surface infiltration reduction approaches evaluated were (1) polymer-modified asphalt, (2) fine-soil cover, (3) buildings (structures), and (4) flexible membrane liners. The engineering study concluded that implementation of these approaches for all of the WMAs ranged from \$40 million to \$158 million. Cost and other factors were the reasons that none of the approaches were implemented.
- On May 4 through 6, 1999 a forum was held in Richland, Washington to discuss techniques for reducing and monitoring infiltration at the SST farms. DOE, Hanford Site contractors, and various vendors from throughout the United States and Canada attended. Pacific Northwest National Laboratory summarized this conference in "Reducing Water Infiltration Around Hanford Tanks" (Molton 1999). Four technical sessions were conducted to discuss (1) moisture monitoring and characterization, (2) structures or buildings to cover the WMAs, (3) surface modifications or covers, and (4) near-surface modifications (barriers and permeability reduction techniques). The forum concluded that existing commercial capabilities could be employed to reduce and monitor infiltration in the WMAs, but that no one technology was appropriate for all seven WMAs. Another conclusion of the forum was that the costs shown in Young et al. (1992) were 50% to 80% higher than those reflected by the vendors attending the forum. During the course of the forum a number of DOE officials and Hanford Site subcontractors addressed site-specific constraints that the vendors may not have taken into account before they submitted their estimated or typical-unit costs.
- In June 2000 DOE revised *Phase 1 RCRA Facility Investigation/Corrective Measures Study Work Plan for Single-Shell Tank Waste Management Areas* (DOE-RL.2000). Section 4.2 of that document identifies a number of general response actions and technology and process options associated with each general response action, and it screens each option based on effectiveness, ability to implement, worker safety, and cost.
- In November 1999 an engineering report by Fluor Federal Services (FFS 1999) was completed. This report was revised and updated in May 2001 (Anderson 2001). In addition to evaluating water lines and wells within the WMAs, the report also evaluated surface water both from natural causes and catastrophic events. Alternatives considered in that report include (1) no action, (2) site grading, (3) geo-fabric liners, (4) asphalt concrete paving, (5) building enclosure with asphalt apron, and (6) run-on

control. The report recommends that a combination of a building enclosure with asphalt apron and run-on control be implemented. While the building enclosure is not the preferred option (because of the cost) the report concludes that it provides the best operational and technical alternative.

Three potentially viable near-term ICMs are: near-surface barriers, surface barriers, and overhead structures. The following sections describe how each of those three near-term ICMs would apply to WMA S-SX.

3.5.2.2 Near-Surface Barrier. A near-surface barrier would consist of an impervious, geo-fabric (geomembrane liner or geosynthetic clay) system over the entire WMA S-SX to direct surface water to the outer boundaries of the tank farms. A run-off collection system consisting of ditches and pipes would be required to route collected surface water to existing drainage routes.

3.5.2.2.1 Implementation at WMA S-SX. Implementation of a near-surface barrier would be disruptive to other tank farm activities. The entire area, 18,000m² (194,000 ft²) at the S tank farm and 20,500 m² (220,000 ft²) at the SX tank farm, would require hand excavation to remove 30 cm (12 in.) of existing soil and subsequent replacement of this soil as a cover over the liner to allow for traffic. The soil would have to be hand excavated because of the tank dome-loading restrictions and the many utilities within the tank farm. Some of those utilities may require support during construction or relocation to a depth below the liner. Installation of the near-surface barrier would require more time than a typical installation because of the many obstructions protruding above the ground surface. During the period that the near-surface barrier is required to control surface water, repairs would be required if any tank farm activities required work below the liner.

3.5.2.2.2 Cost. The estimated costs cited in the engineering study (Anderson 2001) for implementation of a subsurface barrier are \$7.1 million for the S tank farm and \$8.1 million for the SX tank farm.

3.5.2.3 Surface Barrier. The only surface barrier evaluated is a 6 cm (2.5 in.) layer of asphalt cement pavement. Surface barriers that were not evaluated but have been used successfully on other projects include various liquid and solid reagents that are applied and allowed to penetrate the surface materials or are mixed with the surface materials to form a crust. A run-off collection system comprised of ditches and pipes would be required to route collected surface water to existing drainage routes. It is recommended an engineering trade study be conducted to examine the impact an interim surface barrier on tank farm operations would create through the annual interim measures discussions between ORP and Ecology.

3.5.2.3.1 Implementation at WMA S-SX. Implementation of a surface barrier would be disruptive to other tank farm activities. The entire area, 18,000m² (194,000 ft²) at the S tank farm and 20,500 m² (220,000 ft²) at the SX tank farm, would require hand excavation to remove 10 cm (4 in.) of existing gravel cover, which would be taken from the site and disposed of if contaminated or used in the production of the asphalt. The material would have to be hand excavated because of the tank dome-loading restrictions and the many utilities within the tank farm. Some of these utilities may require relocation if they are near the surface following

removal of the 10 cm (4 in.) of existing materials. Installation of the surface barrier would also take additional time from typical installations to seal the numerous obstructions protruding above the surface.

Adequate compaction of both the subgrade and the asphalt will not be obtained because of the obstructions within the tank farm and the tank dome-loading restrictions. During the period that the surface barrier is required to control surface water, traffic loading may do substantial damage to the surface barrier. The cost to repair the asphalt barrier using the special fine mix could be excessive.

3.5.2.3.2 Cost. The estimated costs cited in the engineering study (Anderson 2001) for implementation of a surface barrier are \$3.4 million for the S tank farm and \$3.9 million for the SX tank farm.

3.5.2.4 Overhead Structure. An overhead structure would consist of an enclosed shelter covering the majority of the surface water control area of WMA S-SX. An asphalt apron would be constructed around the perimeter of the structure to capture surface water and route that water to a run-off collection system.

3.5.2.4.1 Implementation at WMA S-SX. Erection of the overhead structure would be more complicated than typical erections because of tank dome-loading limitations. This option may require larger-than-normal cranes for erection of the structure and coverings. To span the entire width of the S or SX tank farm (104 m [340 ft] or 107 m [350 ft], respectively) would limit the weight of equipment that could be attached to the structure (e.g., monorails; lighting; heating, ventilation, and air conditioning). Engineers would have to determine if foundations could be constructed between the tanks at the S and SX tank farms to decrease the free-span distance and to allow greater auxiliary loading of the structure's supports.

The evaluation of which overhead structure to construct must take into account the free-span distances of 104 m (340 ft) and 107 m (350 ft). To provide a structure with this free span, a rigid-framed structure may be required. An evaluation should be made of intermediate supports to be located between the tanks. This would allow the structure to be equipped with accessories that may increase productivity of future tank farm operations (e.g., monorail; lighting; and heating, ventilation, and air conditioning). The use of intermediate supports would also allow the use of enclosure systems other than a rigid-framed structure.

The evaluation of overhead structures should also include recently emerging or advanced technologies (e.g., a domed structure). This technology is purported to provide greater strengths at less cost than conventional structures.

3.5.2.4.2 Cost. The estimated costs presented in the engineering study (Anderson 2001) for implementation of a building enclosure with an asphalt apron are \$18.3 million for the S tank farm and \$20.8 million for the SX tank farm. Depending on the closure technology used at WMA S-SX, a confinement facility would be required (DOE-RL 2000). If a confinement facility were not required, production would be increased 30% by working within an enclosure (Anderson 2001). Credit was not given to these items in determination of the costs.

3.5.2.5 Recommendation. The evaluation of three options in the engineering report (Anderson 2001) resulted in a recommendation to implement the overhead structure. This recommendation is based on the summary of the evaluation criteria that ranked the overhead structure lowest for both S and SX tank farms. The estimated cost for the overhead structure is considerably higher than the other options evaluated and this variation is not well captured. For example, the report did not provide credit for an estimated 30% productivity gain for tank farm operations within the enclosure or that enclosure would be required for certain tank farm closure alternatives.

3.5.3 Additional Potential Interim Corrective Measures

This section identifies additional potential ICMs for consideration at WMA S-SX. These ICMs generally involve a greater commitment of resources than the ICMs discussed in Section 3.5.2 and require a more thorough site-specific evaluation prior to selecting an ICM for implementation at WMA S-SX. Any evaluation of ICMs must include consideration of continued storage of waste in the tanks and future plans to retrieve waste from the tanks as well as cost versus benefits of the technologies in terms of reducing groundwater impacts. If warranted, detailed evaluation of ICMs for WMA S-SX would be conducted in a CMS. Additional potential ICMs are detailed in Appendix F.

3.5.4 Implemented Interim Measures at WMA S-SX

The Tank Farm Vadose Zone Project has implemented the following interim measures at WMA S-SX:

- Installation of water-tight drywell caps
- Abandonment and leak testing of pressurized water lines
- Construction of up-gradient surface water run-on control measures
- Updated and created water line status maps.

3.5.4.1 Installation of Water-Tight Drywell Caps. During the baseline spectral logging of tank farm drywells, the logging contractor, MACTEC-ERS, noted that many of the drywells contained standing water. Review of the well construction records revealed that there was no ready way for this water to enter the bores from the subsurface. Significantly, the drywells used caps that were flush with the ground surface so that would not create traffic obstacles. Consequently, some caps were apparently driven over. Leakage of water ponded on the ground surface within the tank farms into the drywells via broken or leaking surface caps appeared to be a likely cause of standing water in some drywells.

In FY 1999, 786 surface-located drywell caps in the SST farms were replaced with new water-tight surface caps, including those at the S and SX tank farms. These caps were obtained, installed, and inspected as the earliest of the tank farm interim measures. The cost of this activity was \$47,000.

3.5.4.2 Abandonment and Leak Testing of Pressurized Water Lines. The interim measures engineering report (Anderson 2001) identifies four water lines serving WMA S-SX that should be considered for abandonment. An 8-in. water line and a 6-in. raw water line serving the SX tank farm were determined to be unneeded by the CHG cognizant engineer for the SX tank

farm. These lines were cut and capped in April 2001. The CHG cognizant engineer for the S tank farm determined that a 14-in. raw water line and a 4-in. potable water line serving the S tank farm were needed. These lines were leaked tested in May 2001 and determined to not be leaking. These two lines remain in service. The cost of this activity was \$76,000.

3.5.4.3 Construction of Upgradient Surface Water Run-on Control Measures. The interim measures engineering report (Anderson 2001) identifies WMA S-SX as being susceptible to upgradient surface water run-on and ponding. There are two documented incidences of surface water run-on at WMA S-SX. Ponding at the S and SX tank farms was apparent in February 1979 photographs of the effects of rapid melting of snow cover by a Chinook wind. The area of the S and SY tank farms was flooded in 1996 with 2.2 million L (580,000 gal) of water when a 14-in. raw water line broke just east of the SY tank farm. Note that this water line was leak tested in May 2001 and determined not to be leaking.

Upgradient surface water run-on control measures for WMA S-SX were designed in March 2001 and constructed in July 2001. Camden Avenue and 16th Street are to become control measures to route surface water run-on around and down-slope of the farms. These measures consist of a combination of regraded and repaved road surfaces, new curbs and gutters, and a valley drain. The cost of this activity was \$265,000.

3.5.4.4 Updated and Created Water Line Status Maps. Sixteen water line sketch maps indicating the location, water type, pipe diameter, status, and date of installation were included in the interim measures engineering report (Anderson 2001). These maps were field checked and updated by the water purveyor and tank farm engineers and operators. Because an integrated current set of water-line maps for the 200 East and 200 West Areas does not exist, a set of 60 updated water line status maps, including the S and SX tank farms, was released in 2001. The cost of this activity was \$25,000.

3.5.4.5 Decommissioned Unfit-for-Use Wells. The interim measures engineering report (Anderson 2001) identified six wells in the S and SX tank farms that were potential Priority 1 unfit-for-use wells for near-term decommissioning. Priority 1 wells are those dry or abandoned groundwater wells that present the highest risks to groundwater. Many of these wells come into contact with groundwater or are in detrimental locations. Four Priority 1 wells was decommissioned during FY 2000; however, none of these wells were located in WMA S-SX.

3.5.4.6 Technetium-99 in Groundwater. An assessment is planned to determine the appropriateness of an interim measure addressing the elevated concentration of technetium-99 in well 299-W23-19. This assessment will be conducted early in FY 2002 and will consist of two phases.

- **Phase 1:** The well will be restored to its full depth configuration and an aquifer test will be performed to ascertain the aquifer properties at this site and sustainable yield of the well. This phase consists of conducting a step-drawdown test and a short-term (72 hour) active pumping aquifer test followed by a recovery test. The data derived from this test will be analyzed to determine how effective a pump and treat remediation system might be and to provide design input to such a system.

- **Phase 2:** Based on the analysis of Phase 1 data, a long-term (60 to 90 day) periodic (daily) pumping of the well with regular sampling may be carried out. This phase of the testing will be used to help determine the extent and sustainability of the high concentrations of technetium-99.

Based on the results of both Phase 1 and Phase 2, a recommendation will be made on whether or not to proceed with an interim remedial measure (pump and treat) at this site.

4.0 SUMMARY AND CONCLUSIONS OF THE IMPACT (RISK) EVALUATION

An impact evaluation using a suite of numerical simulations was performed to predict long-term human health risks from potential groundwater contamination from WMA S-SX. The evaluation also predicted human health risk at four defined points of compliance using groundwater exposure scenarios. The base case assumes no interim barriers are placed on the WMA before a long-term closure barrier is installed at year 2040. The major sensitivity cases involve placement of an interim barrier over the WMA and the sensitivity of the results to inventory distribution and recharge rate assumptions. The scope and parametric data for these simulations were defined by a modeling data package (Khaleel et al. 2000). This section summarizes results for the 13 simulated cases involving two-dimensional cross-sections through WMA S-SX and one three-dimensional domain of a single tank (quarter symmetry) within the WMA. Risk and dose were evaluated using *Hanford Site Risk Assessment Methodology* (HSRAM) (DOE-RL 1995b) and “Model Toxics Control Act” (MTCA) Method B (unrestrictive) and Method C (industrial) exposure scenarios.

The major findings are described below.

- Predicted groundwater concentrations for technetium-99, nitrate, and chromium exceeded the drinking water standard (40 CFR 141) at the WMA S-SX boundary for all cases except for projected nitrate groundwater concentrations for the two low recharge cases (i.e., 30 and 10 mm/yr).
- Incremental lifetime cancer risk (ILCR) ranges from 9.98×10^{-3} to 8.82×10^{-5} at the WMA S-SX boundary for the industrial worker scenario. The hazard index ranges from 3.0×10^2 to 7.7×10^1 at the WMA S-SX boundary for the industrial worker scenario. Technetium-99 is the key CoC for the ILCR, while chromium and nitrate is the key CoC for the hazard index. Regulatory exceedances are 1.0×10^{-5} for ILCR and 1.0 for hazard index.

Section 4.1 presents the numerical modeling approach. Section 4.2 discusses the numerical simulation results. Section 4.3 presents the human health risk and dose estimation approach. Section 4.4 presents the results of the human health risk and dose estimation evaluation and how these values compare to DQO for WMA S-SX and the regulatory standards. Details on the modeling approach, data used, and numerical simulations are presented in Appendix E.

4.1 NUMERICAL MODELING APPROACH

The numerical simulations were performed with the STOMP (Subsurface Transport Over Multiple Phases) simulator (White and Oostrom 2000a, 2000b). The simulations consider the distribution of contaminants presently in the vadose zone and the migration of the contaminants through the vadose zone to groundwater and to points of compliance within the unconfined aquifer. Four contaminant species (cesium-137, technetium-99, chromium, and nitrate) representing the range of mobile and immobile constituents were considered in the migration and risk analyses. The suite of two-dimensional simulations were used to investigate the impact of the no action alternative (which includes a surface closure barrier); interim surface barriers; water-line leaks; clastic dikes; nonuniform inventories; concentration-dependent density and viscosity for the transporting fluid (i.e., water); and meteoric recharge. A three-dimensional simulation was used to investigate the impact of dimensionality on the numerical predictions.

The simulations do not attempt to model a tank leak itself but model the potential risk posed by past tank leaks, as quantified by existing contamination within the vadose zone. All simulations are composed of steady-flow and transient components, where flow fields developed from the steady-flow component were used to initialize the transient simulation. Steady-state initial conditions were developed by simulating from a prescribed unit hydraulic gradient condition to a steady-state condition, dictated by the initial meteoric recharge at the surface, water table elevation, water table gradient, no flux vertical boundaries, variation of hydrologic properties, and location of impermeable tanks. From the starting conditions, transient simulations of solute transport were conducted for a 1,000-year period (i.e., years 2000 to 3000) that involved changes in the flow fields in response to placement of surface barriers, water-line leaks, or solute-concentration-dependent density and viscosity. All simulations were run assuming isothermal conditions, an assumption supported by the Integration Project S&T activity modeling work (Appendix D). The vadose zone was modeled as an aqueous-gas porous media system, where transport through the gas phase was neglected. All but one simulation used the infinite dilution assumption for coupling fluid flow and contaminant transport. The solute-concentration-dependent density and viscosity run coupled aqueous-phase density with the concentration of a single contaminant, sodium nitrate.

Fluid flow within the vadose zone is described by Richards' equation, whereas the contaminant transport is described by the conventional advective-dispersive transport equation with an equilibrium linear sorption coefficient (K_d) formulation. Detailed stratigraphic cross-sectional models are presented in Appendix E, Figures E.2 through E.4; the models include the effect of dipping strata. The enhanced spreading at the fine-grained/coarse-grained interfaces and the increased down-dip movement of the plume along these interfaces are included in the model.

For two-dimensional cross-sectional models, three representative (west-east) cross-sectional models for the S and SX tank farms (Figure 1.2) are considered:

- Cross-section through tanks SX-107, SX-108, and SX-109
- Cross-section through tanks SX-113, SX-114, and SX-115
- Cross-section through tanks S-104, S-105, and S-106.

Note that, in the discussion below and elsewhere, the three cross-sections are labeled in two ways. For example, the cross-section containing tanks SX-107, SX-108, and SX-109 is often labeled as SX-DD'. Similarly, SX-FF' refers to the cross-section containing tanks SX-113, SX-114, and SX-115; and S-CC' refers to the cross-section containing tanks S-104, S-105, and S-106. Detailed descriptions of individual cases are included in Appendix E, Section E.2.1.

A principal objective of this investigation was to evaluate the effectiveness of interim barriers to the infiltration (recharge) of meteoric water (from winter precipitation and snowmelt) on the migration of contaminants from previous leak sources. The reference suite of simulations (base case) considered the migration of contaminants from field estimates of concentration distributions through the vadose zone and groundwater to the WMA S-SX boundary with no interim barriers but a closure barrier by the year 2040. The timeline for emplacement of the interim and closure barriers and the corresponding recharge estimates used in the base case simulation are indicated in Table 3.1 and also in Appendix E, Table E.1.

Inventory estimates are considered to be a critical factor in calculations, and uncertainties in inventories are considered. The postulated conceptual model uses the recently collected data on technetium-99 and other constituents from borehole 41-09-39, borehole 299-W23-19 near tank SX-115, and the MACTEC-ERS cesium-137 plume data (Appendix E). It is assumed that no tank leaks will occur in the future. Also, it is assumed that, as part of 'good housekeeping,' water-line leaks from existing piping are addressed and resolved. However, as part of sensitivity analysis, simulations are run to evaluate long-term effects of water-line leaks in the vicinity of tank SX-115. The umbrella-shaped dome structure of the tank and shedding of water are simulated. Sediments adjacent to the tanks attain elevated water contents and, while remaining unsaturated, they develop what is known as moisture-dependent anisotropy. Such effects are simulated in the model (Appendix E). Numerical results are obtained for compliance at the WMA boundary, 200 West fence boundary, 200 Area exclusion boundary, and the Columbia River. Except for the 200 West fence boundary, these boundaries are based on DOE-RL (2000). Instead of the 200 West fence boundary, DOE-RL (2000) refers to the 200 Areas boundary. However, since the 200 Areas and the exclusion boundaries are relatively close, the 200 Areas boundary is replaced by the 200 West fence boundary. The focus of the report is at the WMA boundary. Ecology through DOE-FU (2000) required that three additional points of compliance be examined.

Simulation of flow and transport through each cross-section generates a breakthrough curve (BTC) (Appendix E). The temporal and spatial distribution for each of these BTCs are recognized and the principle of superposition is used to generate a composite BTC at the compliance boundary. An analytical/streamline approach is used to route the BTCs through the unconfined aquifer to the compliance boundaries (Appendix E). The BTCs are converted into dose estimates using appropriate factors (Appendix E).

4.2 NUMERICAL SIMULATION RESULTS

A brief description of the simulation cases is provided in Table 4.1. The physical domains for the two-dimensional simulations were east-west sections across the WMA S-SX boundary. These domains were discretized with grid resolutions of 0.5334 m (1.75 ft) in the horizontal direction and 0.4572 m (1.5 ft) in the vertical direction, yielding 42,900- to 48,516-node grids. The simulations involving a clastic dike used grid refinement to include the clastic dike, yielding 50,232-node grids. The physical domain for the three-dimensional simulation was a quarter section of tank SX-108. This domain was modeled at the same grid resolution as the two-dimensional simulations, yielding a 119,422-node grid. Execution times for these simulations varied from 20 to 120 hours, with the longest executions occurring for the three-dimensional simulations and the density- and viscosity-dependent two-dimensional simulations. Mass balance errors over the 1,000-year simulation period for the solute species ranged between $2.06 \times 10^{-7}\%$ to $5.94 \times 10^{-5}\%$ for pressure- and temperature-dependent density and viscosity, and between $2.19 \times 10^{-2}\%$ and $9.83 \times 10^{-2}\%$ for those simulations involving nitrate-concentration-dependent density and viscosity.

Table 4.1. Case Descriptions for the Two-Dimensional Simulations

Case No.	Description*	Interim Barrier	Inventory Distribution	Meteoric Recharge mm/yr
1	Base case (no action alternative)	No	Uniform	100
2	Barrier alternative	Yes	Uniform	100
3	Water-line leak (25,000 gal)	No	Uniform	100
4	Clastic dike	No	Uniform	100
5	Nonuniform inventory	No	Nonuniform	100
6	Nonuniform inventory with barrier	Yes	Nonuniform	100
7	Displaced nonuniform inventory	No	Displaced	100
8	Density and viscosity effects	No	Uniform	100
9	Base case with 50% recharge	No	Uniform	50
10	Base case with 30% recharge	No	Uniform	30
11	Base case with 10% recharge	No	Uniform	10
12	Alternative inventory	No	Alternate	100
13	Water-line leak (200,000 gal)	No	Uniform	100

As indicated earlier, contaminant concentrations at the WMA S-SX boundary were translated to the other three compliance points (i.e., 200 West fence, 200 Area exclusion boundary, and Columbia River shoreline). Simulated results for the base case scenario predicted arrivals of peak concentrations for technetium-99 in the following sequence:

- WMA S-SX boundary, year **2046**
- 200 West fence, year 2181
- 200 Area exclusion boundary, year **2344**
- Columbia River shoreline, year **2545**.

Arrival times for peak concentrations for chromium and nitrate were similar to those for technetium-99; the variations primarily resulted from the initial inventory distributions. Because of its retardation factor and radioactive decay, cesium-137 was undetected at the WMA S-SX boundary for all simulation runs.

Tables 4.2 through 4.4 provide a *summary* of the simulated peak time and concentration for each simulation case for the three species at various compliance points. As described in Appendix E, Tables 4.2 through 4.4 are obtained by combining releases from the three cross-sections using a weighted area approach. Table 4.5 shows the changes in peak concentrations for the three species compared to the base case. Base case area-weighted (Appendix E) BTCs for the three species are shown in Figures 4.1 through 4.3. Note that the slight increase in concentration toward the end of each simulation is due to the assumed increase in recharge rate for the degraded barrier.

Tc-99 Conc. (pCi/L)	WMA S-SX		200 West Fence		Exclusion Boundary		Columbia River	
	Time	Conc.	Time	Conc.	Time	Conc.	Time	Conc.
Case 1	2046	6.85E+04	2181	4.89E+03	2344	3.80E+02	2545	1.28E+02
Case 2	2030	2.90E+04	2179	1.91E+03	2341	1.47E+02	2543	5.11E+01
Case 3	2046	6.74E+04	2180	4.89E+03	2344	3.79E+02	2545	1.29E+02
Case 4	2046	6.83E+04	2181	4.89E+03	2344	3.79E+02	2545	1.28E+02
Case 5	2044	7.49E+04	2179	5.29E+03	2342	4.11E+02	2543	1.39E+02
Case 6	2029	3.44E+04	2178	2.09E+03	2340	1.62E+02	2542	5.61E+01
Case 7	2011	1.71E+05	2149	6.89E+03	2314	5.42E+02	2514	1.78E+02
Case 8	2046	6.92E+04	2180	4.96E+03	2344	3.85E+02	2545	1.30E+02
Case 9	2061	3.53E+04	2203	2.50E+03	2365	1.91E+02	2567	6.67E+01
Case 10	2075	1.74E+04	2223	1.32E+03	2384	9.97E+01	2586	3.54E+01
Case 11	3000*	4.34E+03	2312	3.08E+02	2471	2.26E+01	2673	8.28E+00
Case 12	2046	6.87E+04	2180	4.95E+03	2344	3.84E+02	2545	1.30E+02
Case 13	2047	6.31E+04	2179	4.76E+03	2342	3.68E+02	2543	1.25E+02

*Peak concentrations continue to increase for a 1,000-year simulation period because of the long residence time within the vadose zone for the low recharge rate.

DWS = drinking water standard (40 CFR 141).

Table 4.3. Simulated Peak Concentrations and Arrival Times for Chromium (DWS 50 µg/L) at Various Compliance Boundaries

Cr Conc. (µg/L)	WMA S-SX		200 West Area Fence		Exclusion Boundary		Columbia River	
	Time	Conc.	Time	Conc.	Time	Conc.	Time	Conc.
Case 1	2052	7.33E+03	2191	4.49E+02	2354	3.49E+01	2556	1.19E+01
Case 2	2057	1.02E+03	2210	8.55E+01	2370	6.44E+00	2573	2.31E+00
Case 3	2052	7.34E+03	2191	4.52E+02	2354	3.51E+01	2555	1.20E+01
Case 4	2052	7.30E+03	2191	4.47E+02	2354	3.48E+01	2556	1.18E+01
Case 5	2051	8.71E+03	2188	5.23E+02	2351	4.08E+01	2552	1.38E+01
Case 6	2051	1.29E+03	2205	1.03E+02	2365	7.76E+00	2568	2.77E+00
Case 7	2017	1.49E+04	2157	7.78E+02	2321	6.09E+01	2522	2.02E+01
Case 8	2052	7.42E+03	2191	4.55E+02	2354	3.54E+01	2555	1.20E+01
Case 9	2074	2.04E+03	2226	1.54E+02	2386	1.17E+01	2589	4.14E+00
Case 10	2119	6.38E+02	2272	5.55E+01	2430	4.11E+00	2632	1.50E+00
Case 11	3000*	3.86E+02	3000*	7.27E+00	2771	5.13E-01	2972	1.89E-01
Case 12	2052	7.28E+03	2191	4.51E+02	2354	3.51E+01	2555	1.19E+01
Case 13	2052	7.20E+03	2189	4.55E+02	2353	3.53E+01	2554	1.20E+01

*Peak concentrations continue to increase for a 1,000-year simulation period because of the long residence time within the vadose zone for the low recharge rate.

DWS = drinking water standard (40 CFR 141).

Table 4.4. Simulated Peak Concentrations and Arrival Times for Nitrate (DWS 45,000 µg/L) at Various Compliance Boundaries

NO₃ Conc. (µg/L)	WMA S-SX		200 West Fence		Exclusion Boundary		Columbia River	
	Time	Conc.	Time	Conc.	Time	Conc.	Time	Conc.
Case 1	2041	1.28E+05	2178	9.49E+03	2342	7.37E+02	2542	2.49E+02
Case 2	2029	6.88E+04	2177	4.31E+03	2339	3.34E+02	2541	1.15E+02
Case 3	2041	1.27E+05	2178	9.50E+03	2341	7.38E+02	2542	2.50E+02
Case 4	2041	1.28E+05	2178	9.46E+03	2342	7.35E+02	2542	2.49E+02
Case 5	2038	1.39E+05	2176	1.02E+04	2340	7.96E+02	2540	2.69E+02
Case 6	2027	8.41E+04	2175	4.81E+03	2337	3.73E+02	2539	1.29E+02
Case 7	2007	3.57E+05	2148	1.31E+04	2312	1.03E+03	2513	3.39E+02
Case 8	2041	1.29E+05	2178	9.61E+03	2341	7.47E+02	2542	2.52E+02
Case 9	2058	7.76E+04	2199	5.32E+03	2361	4.09E+02	2563	1.42E+02
Case 10	2074	4.12E+04	2221	3.04E+03	2382	2.31E+02	2584	8.17E+01
Case 11	2167	8.45E+03	2315	7.45E+02	2473	5.48E+01	2676	2.01E+01
Case 12	2039	1.28E+05	2177	9.63E+03	2340	7.48E+02	2541	2.53E+02
Case 13	2041	1.21E+05	2177	9.42E+03	2340	7.30E+02	2541	2.48E+02

Table 4.5. Percent Change in Technetium-99 Peak Concentration as a Percentage of the Base Case 1 (Recharge 100 mm/yr, interim barrier [recharge 0.5 m d yr] by 2010, closure barrier [recharge 0.1 m d yr] by 2040) Peak Concentration

Case No.	Percent Change* in Peak Concentration from Base Case		
	Technetium-99	Chromium	Nitrate
1	100	100	100
	109	119	109
7	249	203	279
12	100	99	100
9	52	28	61
10	25	9	32
11	6	5	7
Barrier Effects with Uniform Inventory			
	42	14	54
6	50	18	66
3	98	100	99
13	92	98	95
4	100	100	100
Density and Viscosity Effects			
8	101	101	101

*Except for Case 6, percent changes for all cases were with respect to the base case. For Case 6, percent changes were ~~with~~ respect to Case 5.

Figure 4.2. Base Case Area-Weighted Average Chromium Concentration versus Time at Compliance Points

Figure 4.3. Base Case Area-Weighted Average Nitrate Concentration versus Time at Compliance Points

The impact of an interim surface barrier was investigated by altering the base case (Case 1) simulation to include an interim barrier in place by the year 2010 (Case 2). Results showed that, with the interim barrier, the peak concentrations were reduced by 58, 86, and 46% for technetium-99, chromium, and nitrate, respectively (Table 4.5). Peak concentrations, translated to the remote compliance points, were similarly reduced. **An** earlier placement of the interim barrier will further delay arrival times and reduce the peak concentrations at the compliance points.

The effect of initial contaminant inventory distributions on BTCs was investigated by varying the base case contaminant inventory distributions. In each of these variations, the integrated quantity of contaminant mass (Ci or kg) was conserved (i.e., held equal to the values reported in Appendix E, Attachment E1). In the first variation (Case 5), the solute mass was concentrated in the region between tanks—the tank ‘umbrella-effect’ region. In the second variation (Case 7), the solute mass **was** concentrated in the region between tanks and displaced toward the water table. In the third variation (Case 12), the solute mass was uniformly distributed over a prescribed circular area below the tanks (i.e., tank diameter). When compared against the uniform distribution, the nonuniform distribution (Case 5) showed little change in peak arrival times and peak concentrations at the four compliance points, primarily because of the homogenizing effect of the Plio-Pleistocene unit. For example, peak concentrations of technetium-99 for the nonuniform distribution (Case 5) at the WMA S-SX boundary were only 9% higher than the base case estimate (Table 4.5). A similar trend was observed for other species (Table 4.5).

The displaced-nonuniform distribution (Case 7) is an extreme scenario that was used to evaluate the effect of the Plio-Pleistocene unit on the BTCs. In this scenario, unlike the nonuniform (Case 5) distribution, the solute mass was displaced well beyond the Plio-Pleistocene unit; the unit has high moisture-holding capacity and consequently a homogenizing effect on the solute front. As expected, the displaced-nonuniform inventory simulations showed markedly earlier peak arrival times and higher concentrations for technetium-99 at the four compliance points. Peak technetium-99 concentration at the WMA S-SX boundary was 149% higher than that for the base case uniform distribution (Table 4.5). For the alternate distribution (Case 12), peak technetium-99 concentration at the WMA S-SX boundary was nearly unchanged compared to the base case (Table 4.5).

To investigate the impact of meteoric recharge on contaminant transport, a series of simulations were performed, using uniform inventory distributions and no interim barriers but having different surface recharge for the first 40 years, compared to the base case (100 mm/yr). Case 9 had a 50 mm/yr recharge rate; Case 10 had a 30 mm/yr recharge rate; and Case 11 had a 10 mm/yr recharge rate. In all cases, the closure barrier was assumed to control recharge beyond the first 40 years. The initial flow field for these simulations was the steady-state condition for the prescribed meteoric recharge rate and fixed groundwater conditions (i.e., water table conditions and gradient). As expected, lowering meteoric recharge delayed peak arrival times and reduced peak concentrations at the compliance points (Table 4.5). The exception was the 10 mm/yr recharge case (Case 11), where arrival times were delayed beyond 1,000 years. However, because of the late arrival, the peak concentrations for the low-recharge case continued to increase for the 1,000-year simulation. Nonetheless, the concentration at the WMA boundary, after 1,000-year simulation, was still well below those for other recharge rates. Figures 4.4 through 4.7 show the recharge effects on technetium-99 BTCs at the first compliance point for various cross-sections. The BTCs followed the expected behavior, with differences among the cross-sections related primarily to how the initial inventories were distributed within the vadose zone. Figure 4.8 is an area-weighted BTC for technetium-99 at the WMA for different recharge cases.

A second suite of simulations was performed for Case 5 (nonuniform inventory) simulation having an interim barrier (Case 6). Results showed responses similar to those for uniform inventory cases with (Case 2) and without (Case 1) an interim barrier. Compared to that for Case 5, Case 6 peak technetium-99 concentration at the WMA S-SX boundary was lowered by about 50% (Table 4.5). Such a reduction was similar to that for uniform inventory cases with (Case 2) and without (Case 1) an interim barrier (Table 4.5).

Figure 4.4. Unaltered Breakthrough Curves for Technetium-99 at the WMA S-SX Boundary for the Three Simulated Cross-Sections (Recharge = 100 mm/yr)

Figure 4.5. Unaltered Breakthrough Curves for Technetium-99 at the WMA S-SX Boundary for the Three Simulated Cross-Sections (Recharge = 50 mm/yr)

Figure 4.6. Unaltered Breakthrough Curves for Technetium-99 at the WMA S-SX Boundary for the Three Simulated Cross-Sections (Recharge = 30 mm/yr)

Figure 4.7. Unaltered Breakthrough Curves for Technetium-99 at the WMA S-SX Boundary for the Three Simulated Cross-Sections (Recharge = 10 mm/yr)

Figure 4.8. Averaged Breakthrough Curves for Technetium-99 at the WMA S-SX Boundary for the Three Simulated Cross-Sections and for Various Recharge Rates

The impact of a soil-saturating water-line leak was investigated by altering the base case simulation to include a water-line leak near the dome of tank SX-I 15. Note that the simulated water-line leak scenarios were not designed to be representative of the leak events that actually occurred near tank SX-I 15 and are discussed in Section 3.4.2. Two water-line leak cases were simulated: 25,000 gal over a 5-day period (Case 3) and 200,000 gal over a 5-day period (Case 13). For the 25,000 gal leak, simulation results showed that this quantity of water was sufficient to saturate the soil between tanks SX-I 14 and SX-I 15, but the plume rapidly diffused as it migrated down through the vadose zone, thus having negligible impact below the Plio-Pleistocene unit. Peak concentrations and arrival times at the four compliance points were essentially unchanged from the base case simulations, demonstrating that the single-event 25,000 gal leak had negligible impact on contaminant migration. For the 200,000 gal leak, leak water migrated over the tank domes and descended rapidly to the groundwater. For the 200,000 gal leak, arrival times were shortened but the shape of the BTCs and the peak concentrations (Table 4.5) were only slightly altered.

Clastic dikes, near-vertical geologic features filled with unconsolidated sediments, have been postulated to form a polygonal pattern in the vicinity of WMA S-SX. The influence of a single clastic dike (Case 4), situated between tanks SX-108 and SX-109, which extended vertically from the base of the tanks to the top of the Plio-Pleistocene unit, was investigated as an alteration to the base case simulation. This suite of simulations used an altered grid for cross-section SX-DD' compared with the base case simulation, where grid refinement was used to include the

clastic dike. Peak concentrations (Table 4.5) and arrival times for technetium-99 for the clastic dike simulations at the four compliance points were nearly identical to those for the base case, demonstrating the negligible influence of a single clastic dike situated outside the initial contaminant inventory domain. Such results for a simulated clastic dike are consistent with other Hanford Site impact assessments (Wood et al. 1995; Mann et al. 2001).

The base case simulations considered the concentration of transported solutes as having no influence on the properties of the carrier fluid (i.e., the infinitely dilute assumption). At the field-measured concentrations, however, the density and viscosity of water is dependent on the concentration of dissolved solutes, especially sodium nitrate. To investigate the influence of concentration-dependent fluid properties, a suite of simulations (Case 8) were performed that varied from the base case in that the aqueous-phase density and viscosity were considered to be a function of the sodium nitrate concentration, as determined by the concentration of dissolved nitrate. Results from these simulations showed nearly same earlier arrival time of the peak concentration and slightly higher peak concentration for technetium-99 at the WMA S-SX boundary (Table 4.5). The chromium and nitrate BTCs showed similar trends. These results indicate that density and viscosity effects have minimal impact on the migration of contaminants through the vadose zone beneath WMA S-SX, partially because of the influence of the Plio-Pleistocene unit.

A three-dimensional simulation of tank SX-108 (modeled in quarter symmetry) was performed to provide a quantitative comparison against the two-dimensional cross-section simulations. To isolate the influence of domain dimensionality, the geology of the three-dimensional domain was developed by extrapolating the east-west cross-section geology in the north-south direction. In addition, the horizontal and vertical grid spacings were unaltered from the base case simulations. The three-dimensional simulation was executed following the base case scenario (i.e., no interim barrier, no water-line leaks, and a closure barrier by 2040). The resulting flow fields and solute migration results at the water table show close agreement compared to the two-dimensional base case simulations (Appendix E). Three-dimensional simulation results indicate that errors associated with analyzing WMA S-SX using two-dimensional cross-sections are minimal for the base case.

The major observations and conclusions, based on the numerical modeling, are as follows.

- The contaminant inventories have a major influence on the peak concentrations and arrival times of long-lived mobile radionuclides and chemical species at the WMA S-SX boundary. Several variations of the inventory distributions were considered. A comparison of the unaltered (i.e., not averaged) BTCs at the first compliance boundary for the three cross-sections suggests that the inventory mass (i.e., Ci or kg) has a much more significant influence on the BTCs than the spatial distribution of the contaminants.
- Recharge estimates have a major influence on the peak concentrations and their arrival times. No tank farm-specific recharge estimates are presently available. The base case infiltration rate of 100 mm/yr was essentially based on lysimeter data for gravel-covered, nonvegetated surfaces that mimic tank farm conditions. Additional studies to better refine the infiltration rates at the tank farms should be considered. Also, because of its

importance, efforts at reducing the current infiltration rates at the tank farms prior to retrieval or closure should be explored.

- The Plio-Pleistocene unit, with its higher moisture-holding capacity and favorable hydraulic properties, can delay migration of contaminants to the water table. The homogenizing effect of the Plio-Pleistocene unit is evident from simulations that considered variations in spatial variability of the vadose zone contaminant inventory. BTCs for cases with nonuniform distribution were similar to those for cases with uniform distribution. While the Plio-Pleistocene unit can prolong the vadose zone residence time, contaminants do eventually break through the unit.
- Limited work on the effect of potential preferential flow paths resulting from clastic dikes suggests that these did not have a major influence on the long-term simulations and BTCs. Such results are consistent with other long-term impact assessments at the Hanford Site.
- The interim surface barriers, as expected, reduce fluxes to the water table. The technetium-99 peak concentrations were reduced by over a factor of two with placement of barriers. Numerical simulation results (Appendix E) suggest that the impact of the interim barrier on lowering peak concentrations is most affected by the location of the initial inventory distribution within the vadose zone.
- Simulated peak technetium-99 concentrations are considerably higher than those measured by the groundwater monitoring wells in the vicinity of the WMA. The measured technetium-99 concentrations for well 299-W23-19 directly east-southeast of tank SX-115 have shown a persistent upward trend (technetium-99 concentration in well 299-W23-19 increased from 39,000 pCi/L in October 1999 to 81,500 pCi/L in March 2001). Numerical simulations (Appendix E) for the base case suggest that peak technetium-99 concentrations for the unaltered (not averaged) BTCs were 4 times (for cross-section SX-FF') to 15 times (for cross-section SX-DD') larger than the highest measured technetium-99 in monitoring wells.

It should be noted that all simulations were run using an isothermal model. Such an assumption is supported by a comparison of simulation results for non-isothermal and isothermal runs (Appendix D). Non-isothermal model simulations indicate that during periods of high heat loads in the fifties and sixties the thermal load from the boiling waste tanks altered flow patterns and caused large-scale redistribution of moisture. As a result, fluid and vapor flow near the high-heat tanks was dominated by vapor-liquid counterflow. Therefore, to understand the historical behavior, it is important to consider the strong coupling between the thermal and hydrologic environments. However, for impact assessment, simulations of technetium-99 migration into the future, on the basis of the current thermal conditions in WMA S-SX, were not significantly different for isothermal and non-isothermal conditions (Appendix D). Nonetheless, for investigations of future tank leaks from retrieval activities (e.g., sluicing), the coupled nature of the thermal and hydrologic environments may have to be considered (Appendix D).

4.3 HUMAN HEALTH RISK AND DOSE ESTIMATION APPROACH

This section presents the approach used to estimate human health risk (risk) and dose associated with exposure to CoCs from past leaks and releases from WMA **S-SX**.

Risk is used herein to refer to the following:

- ILCR, which can occur from exposure to carcinogenic chemicals and radionuclides
- Hazard index, which is a measure of the potential for toxic health effects from exposure to noncarcinogenic chemicals.

Dose is the measure of radioactivity potentially received in a human body.

The interim measures under consideration for WMA S-SX address mitigation of groundwater impacts. The exposure pathways for this risk assessment therefore are based on the groundwater exposure medium. The exposure scenarios used for this assessment are as follows:

- Industrial
- Residential
- Industrial worker
- Residential farmer
- Recreational shoreline user.

Risk associated with the use of groundwater from a hypothetical water supply well was estimated at several downgradient points of compliance over a 1,000-year timeframe. Groundwater contaminant concentration estimates were based on the results of the contaminant transport analysis presented in Appendix E, Sections E.4.0 and E.5.0.

Based on DOE-RL (2000), the risk assessment for this WMA **S-SX** FIR is qualitative at this stage in the corrective action process even though substantial site-specific data have been generated. Qualitative WMA risk evaluations have been performed at the Hanford Site using historical process and characterization data (DOE-RL 1995c; DOE-RL 1996a). These qualitative risk evaluations have been used to initially evaluate the applicability and relative effectiveness of interim measures (e.g., eliminate leaking water lines and replace well caps). The risk assessment presented herein also relies on historical process and characterization data but is supplemented with additional site-specific data collected under the RCRA Corrective Action Program as described in Appendices A and B. The results of this risk assessment are used to support evaluation of potential interim measures or ICMs and to determine the need for additional WMA-specific characterization data.

Procedures for the approach and assumptions necessary to calculate human health risk are described in the following documents:

- “The Model Toxics Control Act Cleanup Regulation” (WAC 173-340), which implements MTCA requirements

- HSRAM (DOE-RL 1995b), which is the risk assessment methodology that DOE, Ecology, and EPA have agreed to use to support Hanford Site cleanup decisions.

The WAC 173-340 implementing regulations define exposure scenarios and input parameters for two types of site uses: unrestricted (MTCA Method B) and industrial (MTCA Method C). Both the Method B and C exposure scenarios include potential consumption of groundwater. The Method B exposure scenario essentially assumes residential use; the scenario has been used in risk assessments of the Hanford Site 100 Areas to represent unrestricted land use (DOE-RL 1995a). The Method C exposure scenario has not been applied for site-specific decisions at the Hanford Site.

Under MTCA, risk assessment requirements for nonradioactive contaminants stipulate that carcinogenic risks shall be less than 10^{-6} (10^{-5} for multiple contaminants) for Method B and 10^{-5} for Method C. Also, concentrations of individual noncarcinogenic contaminants that pose acute or chronic toxic effects to human health shall not exceed a hazard quotient of 1.0.

The MTCA risk criteria apply only to nonradioactive contaminants. The EPA guidance indicates that action is generally warranted when the cumulative carcinogenic risk is greater than 10^{-4} or the cumulative noncarcinogenic hazard index exceeds 1.0. Carcinogenic risks below 10^{-6} or hazard indices less than 1.0 are regarded as 'points of departure' below which no action is required. DOE orders require that groundwater protection standards be consistent with federal and Washington State requirements (i.e., EPA and Ecology requirements).

4.3.1 Receptor Scenario Rationale

DOE and Ecology have agreed (DOE-RL 2000) to use MTCA Methods B and C in the Corrective Action Program. MTCA Methods B and C risks are calculated based on equations and parameters specified in the MTCA protocol for establishing groundwater cleanup levels (WAC 173-340-720). Risk is calculated for the residential farmer, industrial worker, and recreational shoreline user exposure scenarios based on the HSRAM. Estimates of **risk** based on the three HSRAM exposure scenarios are provided in this assessment to allow for comparison to risks cited in *Tank Waste Remediation System, Hanford Site, Richland Washington, Final Environmental Impact Statement* (TWRS EIS; DOE and Ecology 1996) and *Retrieval Performance Evaluation Methodology for the AX Tank Farm* (DOE-RL 1999c). Risk calculations for the three HSRAM-based scenarios use groundwater pathway unit risk factors adapted without modification directly from the TWRS EIS.

Four hypothetical receptor locations identified by DOE and Ecology (DOE-RL 2000) as the points of compliance for which potential risk were calculated are as follows:

- Downgradient WMA boundary
- Downgradient boundary of the 200 West Area
- Downgradient boundary of the 200 Area exclusion zone as defined by the Hanford Future Site Uses Working Group (FSUWG 1992)
- Downgradient at the Columbia River shoreline

For the WMA S-SX boundary, risk and dose is calculated at three separate locations corresponding to the three cross-sections (S-CC', SX-DD', SX-FF') considered in the contaminant transport analysis.

4.3.1.1 Residential Exposure Scenario (MTCA Method B). The MTCA cleanup standards are applicable only to nonradioactive constituents. Under the Method B groundwater cleanup level protocol, exposure to hazardous and carcinogenic chemicals is based solely on ingestion of drinking water (with an inhalation correction factor used for volatile chemicals). Method B risk exposure parameters are discussed in Appendix E, Section E.3.1.1. Method B risk is calculated for the four points of compliance as defined in Section 4.3.1.

4.3.1.2 Industrial Exposure Scenario (MTCA Method C). As in the MTCA Method B residential exposure scenario, the MTCA Method C industrial exposure scenario is applicable only to nonradioactive constituents. Under the Method C groundwater cleanup level protocol, exposure to hazardous and carcinogenic chemicals is based solely on ingestion of drinking water (with an inhalation correction factor used for volatile chemicals). Method C risk exposure parameters are discussed in Appendix E, Section E.3.1.2. Method C risk is calculated for the same four points of compliance as defined in Section 4.3.1.

4.3.1.3 Industrial Worker Scenario. An industrial worker scenario consistent with the scenario described in HSRAM is used to represent potential exposure to workers in a commercial or industrial setting. The receptors are adult employees assumed to work at a location for 20 years. The industrial worker scenario risk exposure parameters are discussed in Appendix E, Section E.3.1.3. The scenario is intended to represent nonremediation workers assumed to wear no protective clothing.

Industrial worker risk is evaluated using a unit risk factor approach consistent with that used for the TWRS EIS and DOE-RL (1999c) analyses. This approach involves calculating risk as the product of the groundwater concentration and the unit risk factor. The calculation equation and unit risk factors are provided in Appendix E, Section E.3.0.

These **unit** risk factors are for the groundwater pathway and are taken **from** the risk analysis presented in the TWRS EIS (DOE and Ecology 1996). These unit risk factors were also used in DOE-RL (1999c). Industrial worker risk is calculated for the same four points of compliance as defined in Section 4.3.1.

4.3.1.4 Residential Farmer Scenario. A residential farmer scenario is used to represent exposures associated with the use of the land for residential and agricultural purposes. This scenario is a slight modification to the residential scenario described in HSRAM; it includes all of the exposure pathways for the residential scenario plus most of the food ingestion pathways described in the HSRAM agriculture scenario. The residential farmer scenario includes using groundwater for drinking water (ingestion rate of 2 L/day [0.5 gal/day]) and other domestic uses as well as for irrigation to produce and consume animal, vegetable, and fruit products. The residential farmer exposure parameters are discussed in Appendix E, Section E.3.1.4.

Residential farmer risk is evaluated using a unit risk factor approach **as** discussed for the industrial worker scenario in Appendix E, Section E.3.1.3. Residential farmer risks are calculated for the same four points of compliance **as** defined in Section 4.3.1.

4.3.1.5 Recreational Shoreline User Scenario. A recreational shoreline user scenario consistent with the scenario described in HSRAM is used to represent exposure to contamination in groundwater seeps along the Columbia River shoreline from recreational swimming, boating, and other shoreline activities. The scenario involves outdoor activities and occurs only in an area within 400 m (0.25 mi) of the river shoreline. The recreational shoreline user scenario exposure parameters are provided in Appendix E, Section E.3.1.5.

Recreational shoreline user risk is evaluated using a unit risk factor approach **as** described in the industrial worker scenario in Appendix E, Section E.3.1.3. Recreational shoreline user risks are calculated only at the downgradient Columbia River shoreline point of compliance that is defined in Section 4.3.1. The recreational land user scenario is not included in the WMA S-SX risk assessment because this receptor does not have access to the groundwater pathways.

4.3.2 Tank Waste Constituents of Potential Concern

Determination of the constituents of potential concern (CoPCs) to be used in the WMA S-SX risk assessment starts with the estimated inventory released from the tank farm system to the environment. That estimated inventory is provided in *Inventory Estimates for SST Leaks in Sand SX Tank Farms* (Jones et al. 2000a). The CoPCs listed in the Jones et al. (2000a) estimate include the analytes listed in the model cited in *Hanford Defined Wastes: Chemical and Radionuclide Compositions* (Agnew 1997). The following sections provide the rationale used to exclude some of these CoPCs to calculate human health risk and dose in the WMA S-SX risk assessment. Because not all of the constituents associated with the released tank waste will migrate to the groundwater, the CoCs in a groundwater pathway must be selected. The rationale for making this constituents selection is provided in the following sections.

4.3.2.1 Rationale for Excluding Constituents of Potential Concern. Following are the criteria used to exclude CoPCs from consideration in the WMA S-SX risk assessment.

- Constituents with distribution coefficients (K_d) equal to or greater than 0.6 mL/g. *Composite Analysis for Low-Level Waste disposal in the 200 Area Plateau of the Hanford Site* (Kincaid et al. 1998) provides reference to distribution coefficient selection used in previous studies and for past tank leaks. *Hanford Immobilized Low-Activity Tank Waste Disposal Performance Assessment* (DOE-RL 1999b), along with Kincaid et al. (1998), provides rationale for selection of CoPCs for risk calculations. Numerical modeling results provided in the TWRS EIS indicate that constituents with distribution coefficients equal to or greater than 1 take over 1,000 years to reach the vadose zone/saturated zone interface. Numerical modeling of past tank leaks for concurrent S tank farm retrieval performance evaluation (Thompson 2001) and for DOE-RL (1999c) indicate that within 1,000 years constituents with distribution coefficients equal to or greater than 0.6 would not reach the underlying aquifer or would reach the underlying aquifer at low concentrations (less than 3.0×10^{-2} pCi/L) that would

not contribute to significant human health risks (less than 4.0×10^{-8} ILCR for the residential farmer scenario) using base case recharge estimates as shown in Table 3.1.

CoPCs eliminated because of the distribution coefficient criterion are aluminum, iron, bismuth, lanthanum, zirconium, lead, nickel, strontium, manganese, calcium, plutonium (total), nickel-59, nickel-63, cobalt-60, strontium-90, yttrium-90, zirconium-93, niobium-93m, cadmium-113m, antimony-125, tin-126, cesium-134, cesium-137, barium-137, samarium-151, europium-152, europium-154, and europium-155, radium-226, radium-228, plutonium series, americium series, curium series, uranium series, and thorium-232.

- Low-activity radionuclides present in low concentrations and with short half-lives if they have decayed for at least five half-lives. A decay time of 5 half-lives is sufficient for decay of 96.9% of the radionuclide activity and results in a reduced level of potential risk (EPA 1995). Based on numerical modeling results provided in the TWRS EIS, constituents with distribution coefficients of 0 take 150 years to reach the vadose zone/saturated zone interface.

CoPCs eliminated because of the half-life criterion are ruthenium-106 and tritium.

- Constituents without documented human health risk or toxicity factors. The basis for these factors is documented in the *Integrated Risk Information System* (EPA 2000a) or the *User's Guide: Radionuclide Carcinogenicity* (EPA 2000b) databases. A constituent lacking a toxicity reference dose or a carcinogenic slope factor is eliminated.

CoPCs eliminated because of the health effects criterion are carbonate, chloride, calcium, hydroxide, potassium, phosphate, sulfate, silica, and sodium.

Although several organic chemicals are listed in the Agnew (1997) model, only EDTA was carried forward because it is the only constituent that has a reference dose. All others were not listed in the Integrated Risk Information System.

In addition, field data were used for revising the risk-producing CoPC (Section 3.3.5) that met the criteria in Section 4.3.2.1, but were determined to have inventories associated with below background levels or very small inventories in the vadose zone. The field data assisted in eliminating the uranium series isotopes (see Section 3.3.5) that appear to be overestimated in Jones et al. (2000a).

4.3.2.2 Constituents of Potential Concern for Risk Assessment. The CoPCs to be used in the WMA S-SX risk assessment after applying the exclusion criteria described in Section 4.3.2.1 are:

- Chemicals: chromium, fluoride, mercury, nitrate, nitrite, and EDTA
- Radionuclides: carbon-14, selenium-79, technetium-99, and iodine-129.

4.3.3 Estimating Total Incremental Lifetime Cancer Risk and Hazard Index

The total ILCR for a particular receptor scenario at a particular point in time and space is expressed as the sum of the ILCR calculated for the individual carcinogenic chemical and

radionuclide CoPCs. Note that because none of the chemical CoPCs identified in Section 4.3.2.2 is classified as carcinogenic, ILCR values for this assessment are based only on radionuclide exposures. Although hexavalent chromium is classified as carcinogenic by inhalation, carcinogenic impacts from hexavalent chromium would apply only for airborne releases from a facility or for suspension of surface contamination. Because groundwater is the only exposure medium considered in this assessment, neither of these exposure routes applies and hexavalent chromium is treated as an ingestion toxicant. As for the total ILCR, the total hazard index is expressed as the sum of the hazard quotients calculated for the individual noncarcinogenic chemical CoPCs. Total ILCR and hazard index values are calculated for each receptor scenario and point of compliance for the 1,000-year period of analysis used in the contaminant transport simulations.

Risks for CoPCs included in the contaminant transport analysis (i.e., technetium-99, nitrate, and chromium) are based on the modeled groundwater concentrations. Risks for CoPCs not included in the contaminant transport analysis are based on scaled groundwater concentrations. Scaling is performed by multiplying the non-modeled CoPC source inventories (as reported in Jones et al. 2000a) by the ratio of the modeled groundwater concentration to source inventory for one of the modeled CoPCs. The basis for the scaling calculations is shown in Table 4.6.

Simulated CoPC	Nou-simulated CoPC Ratioed from Simulated CoPC
Technetium-99	Carbon-14, Selenium-79, Iodine-129
Chromium	None
Nitrate	Nitrite, Mercury, Fluoride, EDTA

4.3.4 Dose Methodology

Radionuclide doses are calculated as the product of the groundwater concentration and a unit dose factor. The unit dose factors used are groundwater pathway unit dose factors provided in Kincaid et al. (1998). Unit dose factors are presented in Appendix E, Section E.3.4. Dose calculations are performed only for the industrial worker exposure scenario. Exposure pathways and parameters associated with this scenario are described in Appendix E, Section E.3.1.3. Industrial worker dose is calculated at the four points of compliance as defined in Section 4.3.1.

4.4 HUMAN HEALTH RISK AND DOSE RESULTS

This section presents the results of the human health risk and dose assessment. The risk and dose values presented are based on the groundwater concentrations generated through contaminant transport modeling (Sections 4.1 and 4.2) and were calculated using the approach described in Section 4.3. Groundwater concentration values from cross-sections S-CC', SX-DD', and SX-FF' at the WMA S-SX boundary are used in Appendix E, Equation E. 19 to calculate the risk and dose values with the methodology described in Section 4.3 and Appendix E, Section E.3.0.

Note that risk and dose results are presented only for a select group of simulation cases (Table 4.7). Results for these cases are representative of the larger set of cases considered in the contaminant transport analysis and include information on the impacts associated with existing conditions (Case 1); interim barrier use (Case 2); and variable meteoric recharge rates (Cases 9, 10, 11). The remaining cases generally represent variations around the existing conditions or interim barrier cases and are not specifically discussed in this section because their impacts are of similar magnitude to either Case 1 or 2.

Case	Description	Rationale
1	Base case (no action alternative)	Reference case. Estimation of impacts from past contaminant releases at WMA S-SX if no interim measures or interim corrective measures were implemented.
2	Barrier alternative and no water-line leaks	Interim corrective measure case. Estimation of degree to which implementation of an interim surface barrier would decrease impacts from past contaminant releases at WMA S-SX .
9	Base case with 50 mm/yr meteoric recharge	Meteoric recharge sensitivity cases. Estimation of degree to which meteoric recharge modeling assumptions affect estimated base case impacts from past contaminant releases at WMA S-SX.
10	Base case with 30 mm/yr meteoric recharge	
11	Base case with 10mm/yr meteoric recharge	

Risk and dose results for the five cases shown in Table 4.7 are presented individually in Sections 4.4.1 to 4.4.5. As discussed in Section 4.3.1, multiple exposure scenarios are considered in this assessment to account for the uncertainty of long-term Hanford Site land use. To simplify the presentation, the individual case discussions focus on the results for the industrial worker scenario. Results for all the receptor scenarios are provided in table format for each case; however, for comparison purposes, a single scenario is sufficient because the relationship between the receptor scenarios remains relatively consistent within each case. For example, regardless of the case or compliance point, the peak residential farmer **ILCR** is always approximately 35 times higher than the peak industrial worker ILCR, and the MTCA Method B peak hazard index is always approximately 2.2 times higher than the MTCA Method C peak hazard index.

4.4.1 Base Case, No Action Alternative (Case 1)

Results for the base case (Case 1) are summarized in Table 4.8. Results for Case 1 reveal three general trends that are also evident in the results for the other cases considered (Cases 2, 9, 10, 11). First, peak values for the cross-sections at the WMA S-SX boundary exceed the peak values for the downgradient compliance points. Second, peak values at the WMA **S-SX** boundary are

highest for cross-sections **SX-DD'** or **SX-FF'**, followed by cross-section **S-CC'**. Third, peak values at the last compliance point (i.e., the Columbia River shoreline) are generally three to four orders of magnitude lower than the peak values at the **WMA S-SX** boundary.

Peak values for Case 1 are the highest of the five cases considered. Between the **WMA S-SX** boundary and the Columbia River shoreline compliance location, the peak industrial worker ILCR varies from 9.98×10^{-3} to 1.33×10^{-6} . Peak ILCR values are driven by technetium-99. The peak industrial worker hazard index varies from 3.00×10^2 to 4.22×10^{-2} . Peak hazard index values are driven by chromium. The peak dose varies from 5.94×10^2 mredyr to 7.94×10^{-2} mredyr. Peak dose values are driven by technetium-99.

Temporal variations in ILCR for Case 1 are shown in Figure 4.9 for compliance points at the **WMA S-SX** boundary and in Figure 4.10 for compliance points between the **WMA S-SX** boundary and the Columbia River. Temporal variations in hazard index and dose for Case 1 are similar to those shown for ILCR. At the **WMA S-SX** boundary, peaks for the three cross-sections arrive within approximately the first 50 years and are all relatively sharp. Peaks at the 200 West fence, 200 Area exclusion boundary, and Columbia River shoreline compliance locations arrive after approximately 180, 350, and 550 years, respectively, and are broader than the peaks at the **WMA S-SX** boundary.

Figure 4.9. Case 1 Industrial Worker ILCR Versus Time at WMA S-SX Boundary

Figure 4.10. Case 1 Industrial Worker ILCR Versus Time at Compliance Points Between the WMA S-SX Boundary and the Columbia River

Table 4.8. Peak Long-Term Human Health Impacts for Case 1

Compliance Point	Residential Farmer		Industrial Worker		Recreational Shoreline User ^a		FETCA Method B ^b		FETCA Method C ^b		Dose to Worker
	ILCR	HI	ILCR	HI	ILCR	HI	ILCR	HI	ILCR	HI	mrem/yr
S-SX WMA Boundary	S - CC'	4.13E-02	5.07E+03	1.15E-03	1.16E+01	N/A	N/A	2.13E+02	N/A	9.75E+01	6.91E+01
	SX - DD'	3.57E-01	2.09E+04	9.98E-03	3.00E+02	N/A	N/A	2.77E+03	N/A	1.26E+03	5.94E+02
	SX - FF'	8.39E-02	6.09E+03	2.34E-03	1.96E+01	N/A	N/A	5.20E+02	N/A	2.38E+02	1.40E+02
200 West Fence		1.82E-03	7.70E+01	5.07E-05	1.60E+00	N/A	N/A	1.32E+01	N/A	6.02E+00	3.02E+00
200 Area Exclusion Boundary		1.41E-04	5.98E+00	3.94E-06	1.24E-01	N/A	N/A	1.02E+00	N/A	4.67E-01	2.35E-01
Columbia River Shoreline		4.77E-05	2.02E+00	1.33E-06	4.22E-02	2.21E-07	4.52E-03	3.48E-01	N/A	1.59E-01	7.94E-02

^aExposures defined to occur only within 400 m (1,300 ft) of the Columbia River shoreline.^bCancer risks not shown because MTCA addresses only nonradioactive contaminants and no nonradioactive carcinogenic chemicals were identified as contaminants of concern for WMA S-SX.

HI = hazard index.

ILCR = incremental lifetime cancer risk.

MTCA = Model Toxics Control Act.

N/A = not applicable.

4.4.2 Barrier Alternative and No Water-Line Leaks Case (Case 2)

Results for Case 2, barrier alternative and no water-line leaks, are summarized in Table 4.9. Results for Case 2 show the same general trends regarding the compliance points as discussed above for Case 1. Peak values for Case 2 are generally a factor of 2 to 10 lower than the corresponding values for Case 1. Between the WMA S-SX boundary and the Columbia River shoreline, the peak industrial worker ILCR varies from 1.65×10^{-3} to 5.30×10^{-7} . Peak ILCR values are driven by technetium-99. The peak industrial worker hazard index varies from 2.99×10^{-1} to 8.79×10^{-3} . Peak hazard index values are driven by chromium and nitrate. The peak dose ranges from 9.85×10^{-1} mrem/yr to 3.16×10^{-2} mrem/yr. Peak dose values are driven by technetium-99.

Temporal variations in ILCR for Case 2 are shown in Figure 4.11 for compliance points at the WMA S-SX boundary and in Figure 4.12 for compliance points between the WMA S-SX boundary and the Columbia River. Temporal variations in hazard index and dose for Case 2 are similar to those shown for ILCR. At the WMA S-SX boundary, peak arrival times for the three cross-sections are similar to Case 1 but the peaks are broader in shape. All three peaks arrive within approximately the first 60 years. Peaks at the 200 West fence, 200 Area exclusion boundary, and Columbia River shoreline compliance locations are also similar to and slightly broader than Case 1 and arrive after approximately 180, 350, and 550 years, respectively.

Figure 4.11. Case 2 Industrial Worker ILCR Versus Time at WMA S-SX Boundary

Figure 4.12. Case 2 Industrial Worker ILCR Versus Time at Compliance Points Between the WMA S-SX Boundary and the Columbia River

Table 4.9. Peak Long-Term Human Health Impacts for Case 2

Compliance Point	Residential Farmer		Industrial Worker		Recreational Shoreline User ^a		MTCA Method B ^b		MTCA Method C ^b		Dose to Worker
	ILCR	HI	ILCR	HI	ILCR	HI	ILCR	HI	ILCR	HI	mrem/yr
S-SX WMA Boundary	S - CC'	2.76E-02	3.43E+03	7.68E-04	5.35E+00	N/A	N/A	1.36E+02	N/A	6.20E+01	4.61E+01
	SX - DD'	5.32E-02	3.35E+03	1.49E-03	2.99E+01	N/A	N/A	3.28E+02	N/A	1.57E+02	8.86E+01
	SX - FF'	5.91E-02	4.11E+03	1.65E-03	9.77E+00	N/A	N/A	3.39E+02	N/A	1.55E+02	9.85E+01
200 West Fence		7.08E-04	3.36E+01	1.98E-05	3.25E-01	N/A	N/A	3.38E+00	N/A	1.55E+00	1.18E+00
200 Area Exclusion Boundary		5.46E-05	2.60E+00	1.53E-06	2.45E-02	N/A	N/A	2.58E-01	N/A	1.18E-01	9.10E-02
Columbia River Shoreline		1.90E-05	9.00E-01	5.30E-07	8.79E-03	8.81E-08	9.60E-04	9.14E-02	N/A	4.18E-02	3.16E-02

^aExposures defined to occur only within 400 m (1,300 ft) of the Columbia River shoreline.^bCancer risks not shown because MTCA addresses only nonradioactive contaminants and no nonradioactive carcinogenic chemicals were identified as contaminants of concern for WMA S-SX.

HI = hazard index.

ILCR = incremental lifetime cancer risk.

MTCA = Model Toxics Control Act.

N/A = not applicable.

4.4.3 Base Case with 50 mm/yr Meteoric Recharge (Case 9)

Results for Case 9, base case with 50 mm/yr meteoric recharge, are summarized in Table 4.10. Results for Case 9 show the same general trends regarding the compliance points as discussed above for Case 1. Peak values for Case 9 are generally a factor of 2 to 4 lower than the corresponding values for Case 1. Between the WMA S-SX boundary and the Columbia River shoreline, the peak industrial worker ILCR varies from 3.03×10^{-3} to 6.92×10^{-7} . Peak ILCR values are driven by technetium-99. The peak industrial worker hazard index varies from 6.73×10^1 to 1.52×10^{-2} . Peak hazard index values are driven by chromium and nitrate. The peak dose varies from 1.50×10^2 mrem/yr to 4.13×10^{-2} mrem/yr. Peak dose values are driven by technetium-99.

Temporal variations in ILCR for Case 9 are shown in Figure 4.13 for compliance points at the WMA S-SX boundary and in Figure 4.14 for compliance points between the WMA S-SX boundary and the Columbia River. Temporal variations in hazard index and dose for Case 9 are similar to those shown for ILCR. Overall, the temporal variations for Case 9 resemble those for Case 2. At the WMA S-SX boundary, peaks for the three cross-sections have slightly delayed arrival times and broader shapes compared to Case 1. All three peaks arrive within the first 75 years. Peaks at the 200 West fence, 200 Area exclusion boundary, and Columbia River shoreline compliance locations are also slightly delayed and broadened compared to Case 1.

Figure 4.13. Case 9 Industrial Worker ILCR Versus Time at WMA S-SX Boundary

Figure 4.14. Case 9 Industrial Worker ILCR Versus Time at Compliance Points Between the WMA S-SX Boundary and the Columbia River

Table 4.10. Peak Long-Term Human Health Impacts for Case 9

Compliance Point	Residential Farmer		Industrial Worker		Recreational Shoreline User ^a		MTCA Method B ^b		MTCA Method C ^b		Dose to Worker
	ILCR	HI	ILCR	HI	ILCR	HI	ILCR	HI	ILCR	HI	mrem/yr
S-SX WMA Boundary	S - CC'	2.76E-02	3.40E+03	7.70E-04	6.29E+00	N/A	N/A	1.40E+02	N/A	6.39E+01	4.63E+01
	SX - DD'	1.08E-01	6.45E+03	3.03E-03	6.73E+01	N/A	N/A	6.95E+02	N/A	3.18E+02	1.80E+02
	SX - FF'	5.81E-02	4.23E+03	1.62E-03	1.19E+01	N/A	N/A	3.58E+02	N/A	1.64E+02	9.69E+01
200 West Fence		9.27E-04	4.20E+01	2.59E-05	5.63E-01	N/A	N/A	5.21E+00	N/A	2.38E+00	1.54E+00
200 Area Exclusion Boundary		7.10E-05	3.22E+00	1.99E-06	4.29E-02	N/A	N/A	3.97E-01	N/A	1.81E-01	1.18E-01
Columbia River Shoreline		2.48E-05	1.12E+00	6.92E-07	1.52E-02	1.15E-07	1.64E-03	1.40E-01	N/A	6.40E-02	4.13E-02

^aExposures defined to occur only within 400 m (1,300 ft) of the Columbia River shoreline.^bCancer risks not shown because MTCA addresses only nonradioactive contaminants and no nonradioactive carcinogenic chemicals were identified as contaminants of concern for WMA S-SX.

HI = hazard index.

ILCR = incremental lifetime cancer risk.

MTCA = Model Toxics Control Act.

N/A = not applicable.

4.4.4 Base Case with 30 mm/yr Meteoric Recharge (Case 10)

Results for Case 10, base case with 30 mm/yr meteoric recharge, are summarized in Table 4.11. Results for Case 10 show the same general trends regarding the compliance points as discussed above for Case 1. Peak values for Case 10 are generally a factor of 2 to 15 lower than the corresponding values for Case 1. Between the WMA S-SX boundary and the Columbia River shoreline, the peak industrial worker ILCR varies from 1.01×10^{-3} to 3.67×10^{-7} . Peak ILCR values are driven by technetium-99. The peak industrial worker hazard index varies from 2.07×10^{-1} to 5.69×10^{-3} . Peak hazard index values are driven by chromium and nitrate. The peak dose ranges from 6.01×10^{-1} mredyr to 2.19×10^{-2} mredyr. Peak dose values are driven by technetium-99.

Temporal variations in ILCR for Case 10 are shown in Figure 4.15 for compliance points at the WMA S-SX boundary and in Figure 4.16 for compliance points between the WMA S-SX boundary and the Columbia River. Temporal variations in hazard index and dose for Case 10 are similar to those shown for ILCR. At the WMA S-SX boundary, peaks for the three cross-sections are further delayed in arrival times and have even broader shapes compared to Case 9. The three peaks arrive within approximately 125 years. The curves for the three cross-sections begin to rise again after approximately 900 years and are still rising at the end of the 1,000-year analysis period. Peaks at the 200 West fence, 200 Area exclusion boundary, and Columbia River shoreline compliance locations are also further delayed and broadened compared to Case 9.

Figure 4.15. Case 10 Industrial Worker ILCR Versus Time at WMA S-SX Boundary

Figure 4.16. Case 10 Industrial Worker ILCR Versus Time at Compliance Points Between the WMA S-SX Boundary and the Columbia River

Table 4.11. Peak Long-Term Human Health Impacts for Case 10

Compliance Point	Residential Farmer		Industrial Worker		Recreational Shoreline User ^a		MTCA Method B ^b		MTCA Method C ^b		Dose to Worker
	ILCR	HI	ILCR	HI	ILCR	HI	ILCR	HI	ILCR	HI	mrem/yr
S-SX WMA Boundary	S - CC'	1.56E-02	1.95E+03	4.36E-04	3.08E+00	N/A	N/A	7.75E+01	N/A	3.54E+01	2.61E+01
	SX - DD'	3.23E-02	1.98E+03	9.02E-04	2.07E+01	N/A	N/A	1.98E+02	N/A	9.03E+01	5.37E+01
	SX - FF'	3.61E-02	2.60E+03	1.01E-03	6.30E+00	N/A	N/A	2.15E+02	N/A	9.82E+01	6.01E+01
200 West Fence	4.88E-04	2.36E+01	1.36E-05	2.11E-01	N/A	N/A	N/A	2.23E+00	N/A	1.02E+00	8.14E-01
200 Area Exclusion Boundary	3.70E-05	1.79E+00	1.03E-06	1.57E-02	N/A	N/A	N/A	1.67E-01	N/A	7.63E-02	6.17E-02
Columbia River Shoreline	1.31E-05	6.34E-01	3.67E-07	5.69E-03	6.10E-08	6.22E-04	N/A	6.02E-02	N/A	2.75E-02	2.19E-02

^aExposures defined to occur only within 400 m (1,300 ft) of the Columbia River shoreline.^bCancer risks not shown because MTCA addresses only nonradioactive contaminants and no nonradioactive carcinogenic chemicals were identified as contaminants of concern for WMA S-SX.

HI = hazard index.

ILCR = incremental lifetime cancer risk.

MTCA - Model Toxics Control Act.

N/A = not applicable.

4.4.5 Base Case with 10 mm/yr Meteoric Recharge (Case 11)

Results for Case 11, base case with 10mm/yr meteoric recharge, are summarized in Table 4.12. Results for Case 11 show the same general trends regarding the Compliance points as discussed above for Case 1. Peak values for Case 11 are generally a factor of 15 to 50 lower than the corresponding values for Case 1. Between the WMA S-SX boundary and the Columbia River shoreline, the peak industrial worker ILCR varies from 5.94×10^{-4} to 8.59×10^{-8} . Peak ILCR values are driven by technetium-99. The peak industrial worker hazard index varies from 1.25×10^1 to 7.54×10^{-4} . Peak hazard index values are driven by chromium. The peak dose varies from 3.26×10^1 mrem/yr to 5.12×10^{-3} mredyr. Peak dose values are driven by technetium-99.

Temporal variations in ILCR for Case 11 are shown in Figure 4.17 for compliance points at the WMA S-SX boundary and in Figure 4.18 for compliance points between the WMA S-SX boundary and the Columbia River. Temporal variations in hazard index and dose for Case 11 are similar to those shown for ILCR. At the WMA S-SX boundary, peaks for the three cross-sections are even further delayed in arrival times and have even broader shapes compared to Case 10. The secondary elevation in ILCR values observed for Case 10 at the end of the 1,000-year analysis period is also observed for Case 11 but is more pronounced. For cross-section SX-DD', the late ILCR peak actually exceeds the earlier peak. Peaks at the 200 West Fence, 200 Area exclusion boundary, and Columbia River shoreline compliance locations are also even further delayed and broadened compared to Case 10 and arrive after approximately 300, 480, and 680 years, respectively.

Figure 4.17. Case 11 Industrial Worker ILCR Versus Time at WMA S-SX Boundary

Figure 4.18. Case 11 Industrial Worker ILCR Versus Time at Compliance Points Between the WMA S-SX Boundary and the Columbia River

Table 4.12. Peak Long-Term Human Health Impacts for Case 11

Compliance Point	Residential Farmer		Industrial Worker		Recreational Shoreline User ^a		MTCA Method B ^b		MTCA Method C ^b		Dose to Worker
	ILCR	HI	ILCR	HI	ILCR	HI	ILCR	HI	ILCR	HI	mrem/yr
S-SX WMA Boundary	S - CC'	3.16E-03	4.08E+02	8.82E-05	7.67E-01	N/A	N/A	1.59E+01	N/A	7.25E+00	5.29E+00
	SX - DD'	1.96E-02	1.12E+03	5.49E-04	1.25E+01	N/A	N/A	1.27E+02	N/A	5.82E+01	3.26E+01
	SX - FF'	8.14E-03	5.94E+02	2.27E-04	1.43E+00	N/A	N/A	4.84E+01	N/A	2.21E+01	1.36E+01
200 West Fence	1.14E-04	5.70E+00	3.19E-06	2.81E-02	N/A	N/A	N/A	3.85E-01	N/A	1.76E-01	1.90E-01
200 Area Exclusion Boundary	8.40E-06	4.19E-01	2.35E-07	2.04E-03	N/A	N/A	N/A	2.81E-02	N/A	1.28E-02	1.40E-02
Columbia River Shoreline	3.07E-06	1.54E-01	8.59E-08	7.54E-04	1.43E-08	8.38E-05	N/A	1.03E-02	N/A	4.73E-03	5.12E-03

^aExposures defined to occur only within 400 m (1,300 ft) of the Columbia River shoreline.^bCancer risks not shown because MTCA addresses only nonradioactive contaminants and no nonradioactive carcinogenic chemicals were identified as contaminants of concern for WMA S-SX.

HI = hazard index.

ILCR = incremental lifetime cancer risk.

MTCA = Model Toxics Control Act.

N/A = not applicable.

4.4.6 Use of Assessment Results for Data Quality Objectives Decisions

Six principle study questions constituting four decision statements are provided in Section 2.0 of Ovink (1999). Those principle study questions are evaluated against the results of the potential risk from Section 4.4.5.

Principal Study Question No. 1 – Do current shallow (less than 4.6 m [15 ft]) soil radionuclide and chemical concentrations resulting from releases within the WMA achieve preliminary corrective measure performance standards for direct exposure in the vicinity of the WMA boundary?

Principal Study Question No. 2 – Do current vadose zone (surface to water table) soil radionuclide and chemical concentrations resulting from releases within the WMA achieve preliminary corrective measure performance standards for groundwater protection in the vicinity of the four potential boundaries (i.e., WMA boundary, 200 Area exclusion boundary, 200 Area buffer zone, Columbia River)?

Principal Study Question No. 3 – Do current groundwater CoC concentrations resulting from releases within the WMA comply with preliminary corrective measure performance standards in the vicinity of the four potential boundaries?

Principal Study Question No. 4 – Is there shallow soil, deep soil, or groundwater information pertinent to ICM technology evaluations that can be collected concurrent with WMA characterization (i.e., opportunities for project integration)?

Principal Study Question No. 5 – Will shallow soil (less than 4.6 m [15 ft]), vadose zone soil (surface to water table), or groundwater radionuclide and chemical concentrations resulting from releases and potential retrieval leak losses achieve closure performance standards in the vicinity of the WMA boundary, 200 Area exclusion boundary, 200 Area buffer zone boundary, and the Columbia River?

Principal Study Question No. 6 – Will shallow soil (less than 4.6 m [15 ft]), vadose zone soil (surface to water table), or groundwater radionuclide and chemical concentrations resulting from releases, potential retrieval leak losses, residual waste, and remaining structures achieve closure performance standards in the vicinity of the WMA boundary, 200 Area exclusion boundary, 200 Area buffer zone boundary, and the Columbia River?

The 200 Area buffer zone was replaced with the 200 Area fence boundary. The shallow soil, vadose zone soil (surface to water table), or groundwater radionuclide and chemical concentrations resulting from releases are above the preliminary performance standards. The current groundwater concentration for technetium-99 is 81,500 pCi/L in well 299-W23-19. The soil concentrations were used as input for the numerical simulation of flow and solute transport modeling. The results of the numerical simulations indicate that the groundwater concentrations would exceed the maximum contaminant levels, and thereby are not protective of groundwater.

The answer to principal study questions 1, 2, 3, 5, and 6 is 'no' at the WMA boundary and 200 West fence; soil and groundwater concentrations would exceed the preliminary performance

standards. The 200 Area exclusion zone boundary and Columbia River would be 'yes.' For principal study question 4, ongoing interim measures and a CMS are proposed for the RCRA groundwater well 299-W23-19 to treat the groundwater for the removal of technetium-99.

4.4.7 Conclusions of Risk and Dose

Table 4.13 presents the peak ILCR, hazard index, and dose for the industrial worker scenario for the five cases analyzed. This comparison indicates the following ranking from the highest risk to lowest risk

- Case 1 (no action alternative)
- Case 9 (base case with 50 mm/yr recharge)
- Case 2 (barrier case with no water lines)
- Case 10 (base case with 30 mm/yr recharge)
- Case 11 (base case with 10 mm/yr recharge).

Case	WMA S-SX Boundary			200 West Fence	200 Area Exclusion Boundary	Columbia River Shoreline
	S-CC'	SX-DD'	SX-FF'			
Industrial Worker Peak Incremental Lifetime Cancer Risk						
1	1.15E-03	9.98E-03	2.34E-03	5.07E-05	3.94E-06	1.33E-06
9	7.70E-04	3.03E-03	1.62E-03	2.59E-05	1.99E-06	6.92E-07
10	4.36E-04	9.02E-04	1.01E-03	1.36E-05	1.03E-06	3.67E-07
Industrial Worker Peak Hazard Index						
1	1.16E+01	3.00E+02	1.96E+01	1.60E+00	1.24E-01	4.22E-02
2	5.35E+00	2.99E+01	9.77E+00	3.25E-01	2.45E-02	8.79E-03
10	3.08E+00	2.07E+01	6.30E+00	2.11E-01	1.57E-02	5.69E-03
11	7.67E-01	1.25E+01	1.43E+00	2.81E-02	2.04E-03	7.54E-04
Industrial Worker Peak Dose (mrem/yr)						
1	6.91E+01	5.94E+02	1.40E+02	3.02E+00	2.35E-01	7.94E-02
2	4.61E+01	8.86E+01	9.85E+01	1.18E+00	9.10E-02	3.16E-02
9	4.63E+01	1.80E+02	9.69E+01	1.54E+00	1.18E-01	4.13E-02
10	2.61E+01	5.37E+01	6.01E+01	8.14E-01	6.17E-02	2.19E-02
11	5.29E+00	3.26E+01	1.36E+01	1.90E-01	1.40E-02	5.12E-03

Rankings by compliance points indicate the following ranking usually occurs (from highest to lowest risk):

- Cross-section SX-DD' at WMA **S-SX** boundary
- Cross-section SX-FF' at WMA **S-SX** boundary
- Cross-section SX-CC' at WMA S-SX boundary
- 200 West fence
- 200 Area exclusion boundary
- Columbia River shoreline.

The CoC driver for **risk** and dose is technetium-99. For the hazard index, the principle CoC drivers are chromium and nitrate.

5.0 CONCLUSIONS

This section summarizes the major findings and conclusions for this report. Areas covered include the overview of the process (Section 5.1), a description of the characterization approach (Section 5.2), a summary of the additions to the characterization database (Section 5.3), a discussion of the affirmation and refinement of the conceptual model for WMA S-SX (Section 5.4), a summary of the simulations and associated impacts analysis (Section 5.5), and a summary of the interim measures already in place.

5.1 OVERVIEW

An extensive characterization and analysis program that evaluates current vadose zone contamination in WMA S-SX has been completed and is described in this document. This work is the culmination of an orderly investigation process that includes the following steps.

1. Collect and interpret available data pertinent to tank leaks and vadose zone contamination.
2. Determine missing information and plan to collect new data and complete analyses.
3. Collect new data through the development of improved sediment collection methods that reduce dose to the workers and improve data quality.
4. Integrate new and old data with numerical modeling of future contamination and associated risk evaluation.
5. Integrate the DOE national laboratories into the effort to better examine the potential for radionuclide transport under the harsh conditions imposed by tank waste leaks.
6. Implement interim measures and/or additional data collection and analysis.

Eight major outcomes have resulted from this work.

- A workable, effective approach has been developed to improve the characterization of vadose zone contamination in the tank farm WMAs, to interpret past contamination events, and to estimate future contaminant migration.
- A set of data collection activities has been completed to fill major data gaps that quantify the nature, extent, and mobility of contamination in the vadose zone. From these data, a conceptualization of contaminant migration events has evolved.
- Through cooperation with the S&T activity of the Hanford Groundwater Vadose Zone Integration Project and other Hanford Site projects, resources normally unavailable to the RCRA Corrective Action Program were put to use on soil and groundwater issues. These activities provided significant insight into their resolution.
- The insertion of DOE national laboratory and university laboratory expertise was directed at important issues and yielded significant results over a very short time period.

- Future migration patterns and associated risk from groundwater contamination have been projected for the next 1,000 years.
- A series of interim measures have been identified and implemented that immediately reduce the potential of accelerated contaminant migration.
- The approach used by the RCRA Corrective Action Program is successful and should be used for future efforts. The approach of the RCRA Corrective Action Program (gather existing data, identify gaps, collect new data based on gaps, analyze the consequence of the data obtained, and document all the efforts) worked extremely well.
- The current conceptual model should be the basis for further RCRA Corrective Action Program activities and modeling.

In addition, some more general conclusions can be reached. These conclusions involve the approach taken by the program itself and the conceptual models used.

The approach, data collection, and analyses also were performed to support other SST programs, specifically the SST Waste Retrieval Program.

Prior to the initiation of the WMA S-SX characterization effort, a conceptual model was developed from the existing data to explain contamination events that lead to the current state of contamination in the WMA S-SX vadose zone and nearby unconfined aquifer. This conceptual model pictured the contaminant transport having two stages (an early stage driven by the chemical constituents of the leak including enhanced moisture flow, followed by a second stage where the natural systems of the vadose zone reasserted themselves). In general, this conceptual model has been strengthened by the new information gathered (Section 5.4).

A second phase of field investigation is not deemed necessary except for the purpose of reducing inventory and migration uncertainty at specific locations identified in Section 6.0. Interim corrective measures related to well 299-W23-19 are ongoing as are interim measures that have been identified by Ecology and DOE. This alleviates the need for an accelerated CMS.

Interim measures that have been implemented will require various monitoring efforts to ensure they are effective. Section 6.0 recommends that the effectiveness of the interim measures that have been performed be monitored and evaluated.

5.2 CHARACTERIZATION APPROACH

The characterization approach to quantify vadose zone soil contamination is identified by three principal factors:

- Collection of field data in areas of known tank leaks
- A tiered sample analysis approach directed at samples affected by tank waste
- Use of laboratory and modeling analyses focused on site-specific processes controlling contaminant movement.

In WMA S-SX, three deep boreholes were completed two to interrogate the vadose zone area contaminated by the tank SX-108 leak (borehole 41-09-39 and SX-108 slant borehole) and one to interrogate contamination from the tank SX-115 leak (borehole 299-W23-19). Innovative techniques were developed to provide minimum disturbance of the soil samples (particularly cross-contamination from other soil depths when attempting to collect from a representative zone), collect highly radioactive samples in a safe manner, and maximize drilling and sampling efficiency. In the SX-108 slant borehole, effective techniques were developed for drilling at an angle and accurately tracking the borehole position to avoid contact with the tank and ancillary equipment. Numerous new procedures were developed to accomplish these tasks because they were new to tank farm operations, and demonstration of worker safety was of paramount concern.

A tiered analysis approach was developed and applied to the collected soil samples with the goal being to locate and characterize contaminant zones containing tank fluid constituents. Sampling sites were selected such that all geologic units and high gamma zones were sampled and the sampling intervals were no more than 3 m (10 ft). Recognizing that the most important data involved the identification and location of tank fluid contaminants in the borehole soil column and that not all samples were going to be contaminated, a core suite of initial screening analyses were performed on all samples. These analyses were convenient and helpful for identification of in situ contamination. These analyses included geologic logging; gamma logging; and water extract chemistry (nitrate concentration, pH, electrical conductivity, total organic carbon, total carbon). If positive results occurred (e.g., high values of chemical constituents), additional analyses were performed to identify specific constituents (e.g., technetium-99). In addition to constituent measurements, some samples were evaluated to elucidate constituent mobility (e.g., cation exchange capacity, distribution coefficient measurements) or hydrologic properties (matric potential, moisture retention curves, saturated hydraulic conductivity).

Laboratory experiments and modeling analyses were conducted that were focused on mechanistic and theoretical explanations of site-specific physical and chemical processes controlling contaminant behavior in the vadose zone. Experimental and modeling results from these studies provided considerable enhancement in the understanding of contaminant behavior and increased confidence in the evaluation of future contaminant behavior and associated risk. This work has been completed by a consortium of researchers from national laboratories and universities organized through the S&T activity that is conducted by Pacific Northwest National Laboratory staff and associated with the Hanford Groundwater Vadose Zone Integration Project and the Environmental Management Sciences Program. Selection of specific research projects was a joint decision resulting from coordination between S&T and Tank Farm Vadose Zone Project staff scientists. The results of these projects for the WMA S-SX characterization effort are provided in Appendix D, with summaries in Sections 3.0 and 4.0 as appropriate.

5.3 PRIMARY ADDITIONS TO THE CHARACTERIZATION DATABASE

A fundamental conclusion from the initial data collection and conceptualization of the current vadose zone contamination was that several aspects of contaminant distribution and mobility in the vadose zone are critical to the successful evaluation of future risk. Furthermore, confidence in the risk evaluation would be greatly enhanced by key additions to the existing database. To improve understanding of contaminant characteristics in the vadose zone, data collection and

various analyses have focused on several key tasks. These tasks include completion of improved total inventory estimates of major tank leak fluids (radionuclides and chemicals), identification of tank leak fluid constituents present in measurable quantities in the vadose zone, and measurements/estimates of contaminant distribution and current mobility in the vadose zone. Given this information and recharge estimates, input parameters to flow and transport models were developed and future groundwater contamination and associated risk estimates were completed.

Inventory estimates of the major tank leaks have been enhanced in two ways.

- Improved inventory estimates were derived from the HDW model providing inventory estimates as a function of time (Section 3.3.1 and Appendix D, Section D.7.3).
- Additional kriging analysis was completed using all of the available cesium-137 concentration data (Section 3.3.1.3). The cesium-137 data included all gamma data from drywells and laterals and all cesium-137 soil sample data from the new characterization boreholes in the SX tank farm.

From this exercise a more refined range of vadose zone cesium-137 inventory, volume discharge, and other contaminants-of-concern estimates has been derived.

Borehole soils analysis data (Section 3.3 and Appendix B, Sections B.2.0, B.3.0, and B.4.0) have clearly identified particular constituents present in the vadose zone from tank leaks and in concentrations large enough to be of concern as future groundwater contaminants. These include technetium-99, chromium, nitrate, and sodium. Comparison of actual cesium-137 concentration measurements with gamma logging data in the SX-108 slant borehole correlate very well (within an order of magnitude), lending confidence to all recent gamma logging measurements. Also, qualitative indications of long-term contaminant mobility were provided by their distribution with depth (e.g., higher concentration zones at greater depth indicate greater relative mobility) and empirical desorption data (e.g., a greater fraction of total contaminant removed by water extraction indicates greater relative mobility). These data indicate which of these constituents are essentially mobile at this time (technetium-99, nitrate); moderately mobile (sodium, chromium); and essentially immobile (cesium-137).

More mechanistically oriented laboratory experiments were conducted to determine the chemical reactions affecting mobility of cesium-137 (and sodium by association) and chromium (Section 3.2 and Appendix D, Sections D.3.0 and D.4.0, respectively). The cesium-137 experiments completed over a range of sodium and cesium-137 concentrations, illustrated that sodium effectively competes for sorption sites with cesium-137 at sufficiently high sodium concentrations. These data, combined with inventory estimates (Section 3.3) and speciation studies (Section 3.3.2 and Appendix D, Section D.7.3), indicate that the initial tank leak composition could have imposed a local chemical environment sufficient to prevent cesium-137 sorption, at least temporarily. Conversely, as sodium concentrations diminish, cesium-137 sorption increases. Soils analyses from the SX-108 slant borehole show a separation of high sodium and cesium-137 concentration zones. These data provide a plausible explanation for the apparently variable cesium-137 mobility in tank SX-108 fluid as it migrated in the vadose zone and the lack of a high cesium-137 mobility period associated with the tank SX-115 leak.

These data also suggest that cesium-137 presently is sufficiently immobile to remain trapped in the vadose zone until radioactive decay reduces the inventory to negligible quantities and should remain so unless some very high-sodium-bearing liquids pass through the contamination zone.

Laboratory experiments and chromium species characterization (Section 3.2 and Appendix D, Section D.4.0) indicate that limited retardation of chromium in the soil column has occurred because iron(II)-bearing minerals reduce chromium from the VI to the III valence state allowing sorption or coprecipitation to occur. Chromium(III) was also measured in soil samples. Laboratory data also indicate that highly caustic solutions dissolved iron(II)-bearing minerals, thereby facilitating the kinetics of chromium reduction.

5.4 AFFIRMATION AND REFINEMENT OF THE CONCEPTUAL MODEL

Before initiation of the WMA S-SX characterization effort, a conceptual model was developed from existing data to explain contamination events that lead to the current state of contamination in the WMA S-SX vadose zone and the underlying unconfined aquifer (Section 2.1.1). The conceptual model aided the selection of field investigations (defined in the workplans) and other pertinent analyses. Additional characterization work and analyses presented in this report affirm the basic tenants of the conceptual model, these being that contaminant migration originating with tank leaks is a two-stage process largely controlled by several key factors including tank waste solution chemistry, vadose zone stratigraphic controls on contaminant movement, natural recharge, and humanmade water discharges (e.g., water-line leaks) to the soil column (Section 2.1.2). During the first stage, now completed, physical and chemical conditions, modified by the leak event were primary drivers on contaminant migration in the vadose zone. In the second and ongoing stage, the tank leak effects have ceased and contaminant migration is controlled by natural processes and, in some cases, accelerated by other manmade events (i.e., leaking water lines).

5.4.1 First-Stage Contaminant Migration

In the area contaminated by the tank SX-108 leak, an outstanding feature of the contamination zone is the extensive distribution of cesium-137 in both the lateral and vertical directions. The additional soil sample analyses from borehole 41-09-39 and the SX-108 slant borehole (Appendix B, Sections B.2.0 and B.4.0, respectively) confirm the occurrence of high cesium-137 concentration zones in the Hanford formation subunit H1 and upper parts of subunit H2 beneath tank SX-108 and extending westward toward tank SX-109. Inventory estimates (Section 3.3; Appendix C, Section C.6.0; Appendix D, Section D.7.3) and geochemical laboratory experiments (Appendix D, Section D.3.0) indicate that local soil chemical conditions imposed by tank fluid chemistry during the first stage created a temporary environment that strongly increased cesium-137 mobility such that it became poorly reactive and migrated with the tank fluid. The primary mechanism for enhanced mobility is the presence of very high sodium concentrations that successfully competed for sorption sites normally occupied by cesium-137. Consequently, cesium-137 is considered to be a marker for tank SX-108 leak migration in the first stage. Also, zones of elevated pH (greater than 8.5) soil water remain that coincide with the high cesium-137 concentration zones and indicate the remnant of high pH tank fluid mixing with moderately alkaline vadose zone soil water. The correlation between the high cesium-137 concentration zone distribution and the distinctive subunit H1 layer indicates the influence of in

situ stratigraphic controls that promote lateral migration, particularly under conditions where high-volume, short-term fluid releases contact horizontal stratigraphic units with contrasting hydrologic properties.

Thermal modeling analyses (Appendix D, Sections D.7.1 and D.7.2) estimate that a high temperature zone area for tanks SX-107, SX-108, and SX-109 existed during the first stage. This zone extended well into the vadose zone below the high cesium-137 contamination zone because of radiogenic heat loading provided by tank waste. The impact of this zone would have been to create an essentially dry zone (ambient temperatures above 100 °C [212 °F]) next to the tank such that local recharge and contaminant migration would have been delayed until the late 1960s.

First stage tank fluid migration is not as clearly defined at the tank SX-115 leak site. Cesium-137 is observed to concentrate under and near the edge of tank SX-115 very close to the assumed leak locations. This distribution indicates that cesium-137 mobility was not enhanced during the first stage and dropped out of solution quickly after tank fluid contacted vadose zone soil. A mechanistic explanation of this observation is provided by inventory estimates of a more dilute solution and the geochemical experimental data suggesting that tank SX-115 fluid chemistry was not sufficient to enhance cesium-137 mobility (i.e., insufficiently high sodium concentrations). Because cesium-137 never experienced a period of high mobility in this area, it does not provide a chemical marker for first stage tank leak migration in the vadose zone. However, the other system components, including a high-volume leak and the underlying subunit H1, are in place to permit large-scale lateral contaminant movement as seen in the vicinity of tank SX-108. Unlike the tank SX-108 site with two boreholes, only one borehole very near the tank is available, preventing evaluation of lateral migration. Given the tank SX-115 waste inventory estimates, a high temperature thermal zone probably occurred near tank SX-115 but should not have been as long-lasting nor extensive as near tank SX-108.

5.4.2 Second-Stage Contaminant Migration

Second-stage contaminant migration is assumed to begin when the physical and chemical effects of a tank leak have dissipated and migration responds to natural environmental or other manmade conditions. In the tank SX-108 area, the tank-leak effects have dissipated, the soil temperatures have reduced sufficiently to allow recharge, and the chemical conditions affecting tank fluid constituents are controlled primarily by ambient soil-water reactions.

Migration is indicated by the variable distribution of tank fluid constituents in the soil samples from both boreholes (Appendix B, Sections B.2.0 and B.4.0). Tank fluid constituents are identified in the borehole soils simply by their presence (e.g., technetium-99 does not occur naturally) or by their presence over some depth interval at elevated concentrations relative to natural levels (e.g., sodium). In the boreholes contaminated by the tank SX-108 leak, the distance between the high cesium-137 versus the high technetium-99/nitrate concentration zones shows second stage contaminant migration. This conclusion presumes that cesium-137 has been essentially immobile during the second stage migration and that technetium-99 and nitrate are chemically nonreactive and moving with the tank fluid. Cesium-137 immobility is indicated by long-term gross gamma logging measurements since 1974 that show only isolated spatial and temporal changes in gamma profiles. Also, current high sodium and cesium-137 concentration

zones are separated by depth and water extraction analyses of borehole soils remove only a small fraction of cesium-137 activity from the soil. Conversely, technetium-99 and nitrate are extracted almost completely from soil by water.

In the tank SX-108 area second stage migration appears to be largely vertical and controlled, in the absence of water-line leaks, by natural recharge. However, several factors hinder quantitative estimates of contaminant migration in this area. These include historical influences of soil heating from high heat tanks, a lack of site-specific recharge rate measurements, and the potential that the Plio-Pleistocene unit is acting as a retarding barrier to vertical migration and enhancing lateral movement. Currently, there is no indication that in the absence of water-line leaks, contaminant migration from tank leaks has extended below the Plio-Pleistocene unit, although eventual migration to the unconfined aquifer is expected (see Section 4.0).

Second stage migration in the area contaminated by the tank SX-115 leak has had a substantially different and more complex history than that in the tank SX-108 area. Elevated pH levels and trace concentrations of cesium-137 in subunit H1 at borehole 299-W23-19 (Section 3.4 and Appendix B, Section B.3.0) suggest that subunit H1 is a plausible starting location for second stage migration at this location.

Subsequently, contaminant migration proceeded at an accelerated rate as indicated by several pieces of data. Most importantly, circumstantial evidence of extensive water-line leakage in the late 1980s to early 1990s, and the continuing occurrence of very large technetium-99 and nitrate concentrations in recent borehole 299-W23-19 groundwater samples (Johnson and Chou 2001; Section 3.1.2.1 and Appendix C, Section C.7.0) suggests that these water-line leaks near tank SX-115 could provide the needed source of water that would explain the rapid contaminant migration rates and high concentration levels for technetium-99, nitrate, and chromium in groundwater at borehole 299-W23-19. Other data indicating enhanced moisture movement in well 299-W23-19 are high moisture contents in borehole soils and matric potential measurements indicating ongoing drainage in the entire soil column. Also, a more pronounced chromatographic separation between chromium and technetium-99/nitrate high concentration zones is observed in borehole 299-W23-19 compared to the tank SX-108 boreholes, suggesting longer recharge times and/or faster recharge rates.

Technetium-99 and nitrate distribution in borehole 299-W23-19 and unconfined aquifer samples also indicate a complex tank fluid migration pattern in the vadose zone. Outstanding features are as follows:

- Maximum technetium-99 and nitrate concentration zones within the Plio-Pleistocene unit
- Much smaller, but still elevated, technetium-99 and nitrate concentrations between the Plio-Pleistocene and the water table.

The obvious discontinuity between technetium-99 and nitrate concentration levels at the bottom of the vadose zone and in the unconfined aquifer show that vertical migration at the location of this borehole (299-W23-19) is not the major contributing pathway. Lateral migration of the primary technetium-99 and nitrate concentration zones to the west of borehole 299-W23-19 is

indicated, with the Plio-Pleistocene unit and perhaps subunit H1 providing stratigraphic control over fluid migration at different times.

5.5 IMPACTS ANALYSIS

In determining potential impacts from soil contamination from past releases, a suite of numerical simulations of flow and solute transport were performed to predict the performance of surface barriers for reducing long-term human health risk from potential groundwater contamination at WMA S-SX. Thirteen simulated cases involving two-dimensional cross-sections through WMA S-SX and one three-dimensional domain of a single tank (quarter symmetry) within the WMA were conducted. The suite of two-dimensional simulations were used to investigate the impact of no action alternative, surface barriers, water-line leaks, clastic dikes, nonuniform inventories, concentration dependent density and viscosity for the transporting fluid (i.e., water), and meteoric recharge. The three-dimensional simulation was used to investigate the impact of dimensionality on the numerical predictions. From the starting conditions, transient simulations of solute transport were conducted for a 1,000-year period (i.e., years 2000 to 3000) that involved changes in the flow fields in response to placement of surface barriers, water-line leaks, or solute-concentration dependent density and viscosity. All simulations were run assuming isothermal conditions. This assumption is supported by the S&T modeling work (see Section 4.2 and Appendix D, Section D.7.2). The vadose zone was modeled as an aqueous-gas porous media system, where transport through the gas phase was neglected. All but one simulation used the infinite dilution assumption for coupling fluid flow and contaminant transport. The solute-concentration dependent density and viscosity run coupled aqueous phase density with the concentration of a single contaminant, sodium nitrate.

Contaminant concentrations at the WMA S-SX boundary were translated to the other three compliance points (i.e., 200 West fence, 200 Area exclusion boundary, and Columbia River shoreline). Simulated results for the base case (no action alternative) scenario predicted arrivals of peak concentrations for technetium-99 in the following sequence:

- WMA S-SX boundary, year 2046
- 200 West fence, year 2181
- 200 Area exclusion boundary, year 2344
- Columbia River, year 2545.

Arrival times for peak concentrations of chromium and nitrate were similar to those for technetium-99, with the variations being primarily due to the initial inventory distributions. Because of its retardation factor and radioactive decay, cesium-137 was undetected at the WMA S-SX boundary for all simulation runs.

Simulation results suggest that two key factors affecting the prediction of contaminant migration are vadose zone contaminant inventory and recharge. The contaminant inventories have a major influence on the peak concentrations and arrival times of long-lived mobile radionuclides and chemical species at the WMA S-SX boundary. A comparison of the simulated BTCs at the first compliance boundary for the three cross-sections suggests that the inventory mass (i.e., Ci or kg) has a much more significant influence on the BTCs than the spatial distribution of the contaminants. Sensitivity analyses indicate that recharge estimates have a major influence on the

peak concentrations and their arrival times. No tank farm-specific recharge estimates are presently available. The base case infiltration rate of 100 mm/yr was essentially based on lysimeter data for gravel-covered, non-vegetated surfaces that mimic tank farm conditions.

The interim surface barriers, as expected, reduce fluxes to the water table. The technetium-99 peak concentrations were reduced by over a factor of two with placement of barriers. Numerical simulation results suggest that the impact of the interim barrier on reducing peak concentrations is most affected by the location of the initial inventory distribution within the vadose zone. Clastic dikes and enhanced fluid properties had negligible impact on simulated peak concentrations.

Overall, modeled peak concentrations exceed the drinking water standards (40 CFR 141) for the mobile constituents (i.e., technetium-99, nitrate, chromium) at WMA S-SX boundary. Exceptions are when recharge is only 30 mm/yr (Case 10) and 10 mm/yr (Case 11) where nitrate values do not exceed drinking water standards. However, tank farm recharges are not expected to be this low. At 200 West Fence, technetium-99 exceeds drinking water standards (40 CFR 141) for all cases, except Case 11 and chromium exceeds drinking water standards for all cases except Cases 10 and 11. Chromium exceeds the drinking water standard for Case 7 (displaced nonuniform inventory) at the 200 Area exclusion zone boundary.

The numerical simulation groundwater concentrations were used to evaluate the human health risk and dose (Section 4.4 and Appendix E, Section E.6.0) at each point of compliance. Five numerical simulation cases were evaluated using five groundwater exposure scenarios. The exposure pathways for this risk evaluation therefore are based on the groundwater exposure medium. The exposure scenarios used for this assessment are as follows:

- Industrial (MTCA C)
- Residential (MTCA B)
- Industrial worker (HSRAM)
- Residential farmer (HSRAM)
- Recreational shoreline user (HSRAM)

The compliance period, exposure scenarios, and compliance points were all established by Ecology and DOE during RFVCMS workshop negotiations in March 1999 (DOE-RL, 2000). Risk associated with the use of groundwater from a hypothetical water supply well was estimated at several downgradient points of compliance over a 1,000-year timeframe. Groundwater contaminant concentration estimates were based on the results of the contaminant transport analysis presented in Section 4.3 and Appendix E, Sections E.4.0 and E.5.0.

Based on DOE-RL (2000), the risk assessment for this WMA S-SX FIR is qualitative at this stage in the corrective action process even though substantial site-specific data have been generated. The results of this risk assessment are used to support evaluation of potential interim measures or ICMs and to determine the need for additional WMA-specific characterization data.

Risks due to contaminants included in the contaminant transport analysis (i.e., cesium-137, technetium-99, nitrate, and chromium) are based on the modeled groundwater concentrations. Risks due to other contaminants are based on scaled groundwater concentrations. Scaling is

performed by multiplying the non-modeled contaminant source inventories (as reported in Jones et al. 2000a) by the ratio of the modeled groundwater concentration to source inventory for one of the modeled contaminants. Because of the suspect amount of tank waste uranium found in the characterization efforts (see Section 3.3.5) and because of the limited mobility of uranium (solubility constraints and the positive distribution coefficient [0.6 mL/g per Kincaid et al. 1998]), uranium was not considered in the risk evaluation.

This impact evaluation indicates that technetium-99 is the key constituent driver for risk and dose, which represents current groundwater impact conditions (see Section 3.3 and Appendix E, Section E.6.0) and chromium and nitrate for the hazard index. For the evaluation between the WMA S-SX boundary and the Columbia River shoreline, the peak industrial worker ILCR varies from 9.98×10^{-3} to 1.33×10^{-6} for the no action base case compared to 1.65×10^{-3} to 5.30×10^{-7} for the barrier case. If the recharge rate is 50 mm/yr, rather than the 100 mm/yr assumed in the no action base case, the peak industrial worker ILCR varies from 3.03×10^{-3} at the WMA boundary to 6.92×10^{-7} at the Columbia River shoreline.

5.6 INTERIM MEASURES SUMMARY

Interim measures are initial response actions that can be taken while characterization activities are underway and long-term strategies are being developed to reduce the impacts of tank leaks on groundwater. Interim measures do not require comprehensive evaluation in a CMS. The ORP and the RPP have actively implemented various interim measures during the time this FIR was being prepared.

The following interim measures have been implemented.

- **Abandon Approximately 1,930 m (6,300 ft) of Active Water Lines.** Pipe breaks, failed leaded joints and poorly functioning gate valves are common. The sitewide failure rate appears to be increasing geometrically. Four pressurized water lines entering the S and SX tank farms from the east were identified and either leak tested or abandoned.
- **Decommission Unfit-For-Use Wells.** Wells and drywells that were identified as unfit-for-use are potential preferential pathways for downward contaminant migration. (Note that many of the wells and boreholes do not extend to the groundwater.) *Engineering Report, Single-Shell Tank Farms Interim Measures to Limit Infiltration through the Vadose Zone* (Anderson 2001) identifies six wells in the S and SX tank farms that are potential Priority 1 candidates for near-term decommissioning.
- **Implement Up-Gradient Surface Water Run-on Control Measures.** Up-gradient surface water run-on control consists of some combination of re-graded ground surfaces, gravel berms, asphalt pavement, and concrete curbs and valley drains constructed outside the SST farms to prevent surface water from pressurized water-line leaks and unusual meteorological events from flowing onto the tank farm areas. The report recommends that run-on control be established to prevent surface water from entering the SST farms from outside sources, even if no other interim measures are selected to reduce infiltration within each SST.

6.0 RECOMMENDATIONS

This section provides recommendations for further investigations and decisions based on findings from the WMA S-SX vadose zone and groundwater characterization activities. Recommendations for further investigations and decisions are provided for the following:

- Interim measures
- Accelerated CMSs
- Future tank farm operations
- Collection of additional data and information
- Lessons learned
- Restructuring of the RCRA Corrective Action Program.

6.1 RECOMMENDATIONS FOR INTERIM MEASURES

As discussed in Section 3.1.2, artificial recharge sources can have an important impact on contaminant transport. Interim measures are already being implemented at WMA S-SX (see Section 3.5):

- Groundwater wells have been capped and some decommissioned
- Water lines into the S and SX tank farms have been either cut or leak tested
- Berms and gutters are being constructed around the S, SX, T, TX, TY, and U tank farms to lessen potential water run-on.

Other interim measures are planned (e.g., well decommissioning) to mitigate the artificial recharge. These interim measures should be incorporated throughout the tank farms to ensure that best management practices are incorporated to prevent run-on and run-off water and reduce potential driving forces that cause contaminants to migrate downward to the groundwater. In addition, waterlines that are deemed necessary should be leak tested on a periodic (i.e., annual) basis.

6.2 ACCELERATED CORRECTIVE MEASURE STUDIES

According to HFFACO Milestone M-45-58 (Ecology et al. 2001), a CMS could be conducted after the RFI report is written if determined to be needed by Ecology. The date for issuance of the CMS is to be determined.

The major potential corrective measures are the removal of waste, thus eliminating the source, and the mitigation of artificial recharge through run-on controls and leaking water lines (Sections 3.5 and 6.1). As proposed in HFFACO Change Package M-45-00-01A (Ecology et al. 1989), waste from two tanks in the S farm (i.e., tanks S-102 and S-112) will be retrieved and sent to double-shell tanks in 2006 thus beginning the process of waste removal.

Corrective measures to remove soil or piping are not recommended even though surface contamination (less the 4.6 m [15 ft] bgs) is widespread. Because of concerns for tank structural integrity, load limits exist for any operations inside the tank farms. Such load restrictions greatly

limit options for removing soil. In addition, soil removal could not be conducted without considering removal of the ancillary equipment piping systems throughout the tank farms that connect the tanks. Removal of these pipes would have to be conducted in unison with soil removal activities. The removal of the ancillary equipment piping would expose workers to significant radiation.

Water lines serving WMA S-SX are being cut and capped. Run-on and run-off controls have been implemented. Construction of long-term surface barriers is planned at the time of tank farm closure, depending on the closure strategy chosen.

A possible accelerated interim measure would be the placement of interim barriers. Numerical simulation results summarized in Section 4.2 suggest that compared to the no action alternative, placement of an interim surface barrier provides very little reduction in peak concentrations for mobile contaminants. It is premature to implement additional interim measures such as an interim surface barrier until the impact of capping water lines and run-on and run-off barriers can be ascertained and documented. If closure of the tank farms is delayed, safety issues associated with an interim barrier that could increase exposure to workers during waste retrieval efforts must be balanced against long-term environmental concerns. An engineering study for placing an interim surface barrier on tank farms should be conducted to determine the costs and impacts on tank farm operations and waste retrieval actions. Thus, an accelerated CMS is not recommended at this time.

6.3 FUTURE TANK FARMS OPERATIONS

Future tank operations (i.e., those at WMA S-SX and other tank farm WMAs) can benefit from the information gained from the WMA S-SX waste characterization studies in the following areas:

- Storage operations (e.g., waste transfers)
- Integration among waste retrieval, tank farm closure, and RCRA Corrective Action Program activities
- Matric potential and moisture content measurements in other SST farms.

Numerous tank waste leaks have occurred in the SST farms through overfilling of tanks or through leaks in ancillary equipment (e.g., piping) during transfers of waste from one tank to another. This characterization program has shown how important the effects of anthropomorphic type leaks from tank infrastructure have been in the migration history of tank leaks. Therefore, aboveground piping and similar types of best management practices should be used during waste retrieval activities to minimize potential releases to the environment in the future during waste retrieval activities.

Tank waste retrieval and tank farm closure decisions are partially based on information obtained from past leaks that occurred in the SST farm system. The RCRA Corrective Action Program characterization activities quantify vadose zone contaminant characteristics caused by past leaks and provide a better understanding of the environmental parameters (both human-made and natural) affecting contaminant migration. This information provides a means of estimating the

consequences of other leaks that may occur during retrieval and after closure. This capability is useful for determining the best approaches for waste retrieval and closure that satisfy regulatory requirements and are cost effective. Already, the Retrieval Program is using the data (particularly the data modeling package) from the Characterization Program in analysis of the impacts from potential leak losses in tanks S-102 and S-112. Greater integration is projected for the future as waste retrieval activities increase.

The new enhanced understanding of cesium migration implies that new sodium sources should not be applied to the vadose zone. Without such sources, the cesium-137 is not expected to move significant distances. Thus, future liquid waste retrieval activities should evaluate the use of either limited water-based or dry waste retrieval methods instead of sodium-rich supernate as the waste retrieval media to ensure cesium does not migrate further downward, especially on known past leaking tanks like tank SX-115.

6.4 COLLECTION OF ADDITIONAL WMA S-SX DATA AND INFORMATION

Additional data collection is warranted only if the data collected are anticipated to have a significant impact on the findings presented in this report. Additional data do not appear to be necessary to support interim action decisions.

To reduce uncertainty, additional data could be obtained in WMA S-SX:

- Quantify gamma activity directly beneath the tanks through the use of the laterals located beneath SX farm tanks
- Quantify recharge rates for tank farm sediments
- Obtain vadose zone samples near tanks SX-107, S-104, and SX-115 and analyze those samples for important contaminants.

Horizontal access tubes (laterals) that were used for gross gamma and moisture measurements exist approximately 3 m (10 ft) beneath 10 of the SX farm tanks (tanks SX-105, SX-107, SX-108, SX-109, SX-110, SX-111, SX-112, SX-113, SX-114, SX-115). These laterals should be re-used for spectral gamma, moisture, and temperature measurements. If possible, contaminated soil samples may be retrieved.

The matric potential and moisture content measurements for sediment samples in WMA S-SX are valuable in determining the tank farm soil moisture regime and potential for contaminant migration (see Section 3.1.2 and Appendix C). These measurements can and should be extended to other *tank* farms. In FY 2001, a plan similar to that used for analyses of gross gamma measurements was developed to analyze previously collected moisture content measurements. Such analyses should be performed for all SST farms to aid in identifying preferred migration pathways.

Tank SX-107 may have leaked about 24,000 L (6,350 gal), about 40% of the amount that leaked from tank SX-108. However, most of these contaminants are thought to have moved almost vertically, not extending much beyond the edge of the tank. Tank SX-107 is a candidate for further investigation.

The only new characterization performed in the S tank farm was that using a cone penetrometer to detect gamma radiation and the retrieval of a few soil samples. Given the presumed leak volume of 90,800 L (24,000 gal), additional soil sample gathering at depth is indicated with subsequent contaminant analysis to provide data to support future waste retrieval activities (see Section 3.3 and Appendix B, Section B.6.0).

Technetium-99 concentrations in groundwater at well 299-W23-19 near tank SX-115 (the greatest manifestation of contamination in groundwater due to a tank waste source) are much higher than supported by a vertical pathway through the vadose zone. The groundwater data, stratigraphic conditions, leak characteristics, and current aquifer gradient all point toward a contaminated vadose zone in the Ringold Formation west of well 299-W23-19. In addition, a second characterization borehole would provide information on contaminant transport, similar to the pair of holes near tank SX-108.

6.5 LESSONS LEARNED

Much has been learned from the characterization, laboratory analyses, and modeling done for WMA S-SX. For example, the drilling techniques developed from the SX-108 slant borehole may be applied to characterization of the TX tank farm. The use of a tiered analysis approach has greatly decreased costs while prioritizing areas of greatest interests. Finally, non-isothermal and isothermal modeling (Appendices D and E) have improved the assessment of future releases to the groundwater and an understanding of thermal effects for contaminant migration through the vadose zone.

The main lesson learned is that the approach used in creating this FIR was successful and should be repeated for other FIR efforts. The FIRs will provide the baseline information to support tank waste retrieval and tank farm closure. The steps used in the approach are as follows:

- Collect geophysical data from previously published reports
- Collect and document construction and operational history
- Document the state of knowledge through a subsurface conditions description report (Johnson et al. 1999)
- Perform and document a DQO process (Ovink 1999) to prioritize new data collection activities
- Document the new work to be done in a work plan addendum (Henderson 1999; Rogers and Knepp 2000)
- Implement and document the work plan addendum (drilling, sample collection, geophysical logging, and laboratory analyses) (Henderson 1999; Rogers and Knepp 2000)
- Perform and document additional data gathering and analysis activities

- Work with others (e.g., Integration Project S&T activity) to gather and document additional data gathering and analyses activities
- Plan, perform, and document computer modeling (Khaleel et al. 2000; White et al. 2001)
- Integrate and document the preceding activities in a FIR.

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APPENDIX A

WORK PLAN INVESTIGATIVE APPROACH

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LIST OF TERMS

bgs	below ground surface
CHG	CH2M HILL Hanford Group, Inc.
DQO	data quality objectives
Ecology	Washington State Department of Ecology
PNNL	Pacific Northwest National Laboratory
RCRA	<i>Resource Conservation and Recovery Act of 1976</i>
WMA	waste management area

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A.I.O INTRODUCTION

This appendix summarizes the two work plans for waste management area (WMA) **S-SX**: *Preliminary Site-Specific SST Phase 1 RFI-CMS WorkPlan Addendum for WMA S-SX* (Henderson 1999) and *Site-Specific SST Phase 1 RFI/CMS WorkPlan Addendum for WMA S-SX* (Rogers and Knepp 2000). The activities defined in the two work plans have been completed.

Both Henderson (1999) and Rogers and Knepp (2000) are intended to serve as guidelines for the work described and are designed to allow for changes depending on conditions encountered in the field. **Any** changes were recorded on the appropriate field documentation, memoranda, or letters. **Any** modifications that did occur are addressed in Appendix B.

The activities performed in accordance with the work plans were **as** follows:

- Borehole 41-09-39 sampling and decommissioning
- *Resource Conservation and Recovery Act of 1976* (RCRA) groundwater monitoring well sediment sampling and analyses
- Installation of new borehole (299-W23-19) at tank SX-115
- Installation and decommissioning of new slant borehole at tank SX-108
- Near-surface characterization in the S tank farm.

The following sections discuss these activities.

A.2.0 BOREHOLE 41-09-39 DECOMMISSIONING

Borehole 41-09-39 was driven to 40.1 m (131.5 ft) below ground surface (bgs) in December 1996 in the **SX** tank farm. A 17.8 cm (7 in.) outside diameter by 16.5 cm (6.5 in.) inside diameter well casing was placed from ground surface to 39.8 m (130.5 ft) bgs. The casing was initially closed at the bottom with a steel plug. The bottom plug was milled out and borehole 41-09-39 was extended to 69 m (225.3 ft) bgs in September 1997. A second 11.4 cm (4.5 in.) outside diameter by 9.8 cm (3.8 in.) inside diameter casing string was installed inside the 17.8 cm (7 in.) casing. The casing is 65 m (214 ft) in length by 11.4 cm (4.5 in.) outside diameter steel pipe, with a 3 m by 8.9 cm (10 ft by 3.5 in.) 0.010 slot stainless steel screen with a 0.3 m by 8.9 cm (1 ft by 3.5 in.) blank for a total length of 69 m (225 ft). There is no annular seal in either section of casing strings.

Borehole 41-09-39 decommissioning activities included sidewall sampling in the upper portion of the borehole; that is, 39.6 m (103 ft) bgs to surface. The lower portion of borehole 41-09-39 was sampled in 1997 and 1998. The following are the field activities executed as part of borehole 41-09-39 decommissioning:

- Removed Kabis sampler to support decommissioning
- Performed groundwater sampling and analysis before decommissioning
- Performed a tracer test that might clarify path, direction, and rate of groundwater flow
- Measured formation in the open borehole face as the casing is removed and measured temperature in the casing prior to removal to correlate sediment temperatures for future investigations
- Conducted borehole geophysical logging and analysis (moisture, neutron spectral gamma, and high-purity germanium analysis) to find indicated zones of contamination and stratigraphic correlation
- Sampled at intervals in the driven portion of the borehole to try to determine if drag-down from original drilling may be the cause of contamination found during geophysical analysis
- Obtained sediment samples to analyze for presence and concentration of contaminants and to evaluate alterations of the sediments from waste chemistry effects
- Obtained sediment samples to support preparation of the borehole geologic logs and stratigraphic and lithologic contact correlation with other boreholes
- Respond to the Washington State Department of Ecology (Ecology) and *Washington Administrative Code* requirements to decommission the borehole in a compliant manner.

The way some or all of the work was executed may have been modified because of field conditions; such modifications are acceptable per Henderson (1999). Any changes will be recorded on the appropriate field documentation, memoranda, or letters.

A.2.1 REMOVAL OF KABIS SAMPLER

The Kabis sampler is 10.2 cm (4 in.) in diameter and stuck at the top of the 7.6 cm (3 in.) well screen section (Johnson and Chou 1999). The sampler was removed using appropriate techniques. After removing the sampler; the 11.43 cm (4.5 in.) borehole casing was brushed and swabbed to improve the ability to gather high-purity germanium logging runs.

A.2.2 GROUNDWATER ANALYSES

The collection and analysis of groundwater samples from borehole 41-09-39 was completed before initiating the decommissioning activities described in Henderson (1999). Therefore, details of the groundwater analyses work are not addressed in this appendix. Information regarding groundwater analyses may be found in *RCRA Assessment Plan for Single-Shell Tank Waste Management Area at the Hanford Site* (Johnson and Chou 1999).

A.2.3 TRACER INJECTION TEST

The purpose of the tracer injection test was to measure direction and flow rate of the groundwater from the center of the SX tank farm to monitoring wells surrounding the tank farm. The tracer medium was sodium bromide powder dissolved in 15,140 L (4,000 gal) of water to obtain a 50 parts per million bromide solution. The well screen sections remain in the borehole to ensure that the hole stays open and to provide better control over the injection zone and the rate of injection for the tracer test. Removal of the screen could create downhole conditions that could prevent completion of tracer testing and complicate the decommissioning process. A variance request to leave the screen in the borehole was approved by Ecology.

A.2.4 BOREHOLE GEOPHYSICAL SURVEYING ACTIVITIES

Borehole 41-09-39 was geophysically surveyed in the lower portion prior to removal of the 11.43 cm (4 in.) casing and in the upper portion of the borehole prior to removal of the 17.8 cm (7 in.) casing to provide additional characterization information to supplement the sediment sampling data for the entire borehole. The following geophysical surveying techniques were used during borehole 41-09-39 decommissioning:

- Gross gamma logging to identify confining layers and for stratigraphic correlation
- Spectral gamma logging for measuring the distribution of selected radionuclides
- Neutron log for measuring the saturation distribution
- Neutron-enhanced spectral gamma logging for correlation of high-salt tank waste and moisture content with spectral gamma and neutron probes, respectively
- Infrared temperature gauge for measuring sediment temperature (this logging will be conducted both inside and outside the conductor casing for future correlation analysis).

The existing equipment and procedures for gross gamma and spectral gamma logging in use at the Hanford Site provide acceptable data through the various quality assurance measurements.

A.2.5 SIDEWALL SAMPLING BOREHOLE SEDIMENTS

Sixteen sidewall sample locations have been identified in accordance with the data quality objectives (DQO) process. Prior to sample collection, comparison of the geophysical surveys obtained from activities specified in Section A.2.4 to the surveys utilized in the DQO meeting was done to verify sample locations. If the geophysical surveys indicated movement of the gamma contamination or changes in moisture content, the sample horizons were adjusted with the concurrence of the CH2M HILL Hanford Group, Inc. (CHG) technical representative. The sample locations are identified in Table A.1. Three samples were taken in a 120° radial pattern at each sample horizon at the bottom of the 11.43 cm (4.5 in.) casing for a total of 48 aliquots. Samples were retrieved using a sidewall sampler.

Table A.1. Sample Number, Sample Interval, and Geologic Medium for Sampling During Decommissioning of Borehole 41-09-39 as Determined in the Data Quality Objectives Process

Sample Number	Sample Interval Below Ground Surface (ft)^a	Geologic Medium
1	39.9 – 40.2 m (131 – 132)	Silt – Plio-Pleistocene unit
2	35.7 – 36.0 m (117 – 118)	Silty sand – Hanford formation
3	34.1 – 34.4 m (112 – 113)	Silty sand – Hanford formation
4	32.9 – 33.2 m (108 – 109)	Silty sand – Hanford formation
5	31.1 – 31.4 m (102 – 103)	Silty sand – Hanford formation
6	29.0 – 29.3 m (95 – 96)	Sandy gravel – Hanford formation
7	27.1 – 27.4 m (89 – 90)	Sandy gravel – Hanford formation
8	25.0 – 25.3 m (82 – 83)	Gravelly sand – Hanford formation
9	24.1 – 24.4 m (79 – 80)	Gravelly sand – Hanford formation
10	22.6 – 22.9 m (74 – 75)	Gravelly sand – Hanford formation
11	21.0 – 21.3 m (69 – 70)	Gravelly sand – Hanford formation
12	19.8 – 20.1 m (65 – 66)	Slightly silty sand – Hanford formation
14	17.4 – 17.7 m (57 – 58)	Slightly silty sand – Hanford formation
15	13.7 – 14.0 m (45 – 46)	Gravelly sand – original backfill ^b
16	7.6 – 7.9 m (25 – 26)	Gravelly sand – original backfill ^b

If sampling the sidewall produced no sample or a limited sample collection as a result of sidewall collapse or poor retrieval as a result of field conditions, a split-spoon sample was to be collected if sidewall collapse occurs. If corrected sample volumes were small, another sample was to be attempted at an appropriate location above the first attempted sample location, unless interference for the next specified sample was a concern. See Appendix B for discussion of the events.

Once received at the laboratory, the samples underwent the analysis scheme identified in Figure A.1, using the analytical methods listed in Henderson (1999). This analysis event produced few samples with limited sample volume. Therefore, hold points were inserted into the process to allow the laboratory and CHG technical staff to collaborate and review data before each new round of analyses. See Appendix B for reports of the data review activities.

Based on the results of the primary analyses, spectral gamma surveys, and moisture content measurements performed during the field geophysical surveys and the geologic logging and field notes, geological technical experts, CHG technical staff, the laboratory technical staff, and decision-makers (Ecology and the U.S. Department of Energy) convened to determine what additional analyses should be conducted. Some of the determining criteria were to be the amount and integrity of the remaining sample, primary analytical results, and regulatory requirements. Based on these decisions, the secondary and tertiary analyses were to be performed. See Appendix B for report of the analyses performed.

A.2.6 REMOVAL OF THE OUTER TEMPORARY CASING

The total length of the 11.43 cm (4.5 in.) outside diameter casing removed is 63.4 m (208 ft). The casing shoe has a 13 cm (5 in.) outside diameter. Sediment sampling **was** conducted in 1997 from 39.6 m to 68.9 m (130 ft to **225** ft) bgs; therefore, no sampling was required in this interval. Abandonment of the interval is in compliance with “Minimum Standards for the Construction and Maintenance of Wells” (WAC 173-160) requirements. After the decommissioning, all steel casing in the borehole was removed and transferred to an appropriate disposal facility or a controlled decontamination facility.

Figure A.1. Analytical Scheme for Analysis of Borehole 41-09-39 Samples

A.3.0 RESOURCE CONSERVATION AND RECOVERY ACT GROUNDWATER MONITORING WELL SEDIMENT SAMPLE ANALYSIS

Continuous split-spoon driven samples and drill cutting samples were collected in conjunction with the installation of three RCRA groundwater monitoring wells. The southern-most monitoring well is located about 50 m (164 ft) southeast of *tank* SX-I 13 (Figure A.2). From this well, continuous sediment split-spoon driven samples from about 6 m (20 ft) bgs to refusal (anticipated to be near the top of the Ringold Formation) were collected. Drill cuttings were collected from refusal to the total depth of the water table. The other two RCRA groundwater monitoring wells are located east of the S and SX *tank* farms. Drill cuttings were collected from these two wells. Selected portions of the driven samples and cuttings were analyzed for chemical and physical characteristics. A detailed description of the work associated with the installation of these monitoring wells has been developed and, once Ecology comments are incorporated, will supercede Johnson and Chou (1999). Only details associated with analysis of sediment split-spoon driven samples and cuttings are addressed in this appendix.

Continuous driven samples taken from the vadose zone during construction of one well (well 3 of Figure A.2), and the samples were made available for hydrologic properties analysis. The analyses required for this sample are listed in Table A.2. Samples for analysis were from each stratigraphic unit, stratigraphic contacts, weathered bedding structures, and lithologic facies changes.

Figure A.2. Locations for the New Borehole and Resource Conservation and Recovery Act Groundwater Monitoring Wells

Analysis/ Constituent	Preparation Method	Preparation Procedure Number	Analytical Method	Analytical Procedure Number*
PH	Water extract	Methods of Soil Analysis, Part 2; 62-1.3.2.2	Electrometric	Methods of Soil Analysis; 60-3.4
Particle size distribution	Bulk sediment	NA	Particle size distribution	ASTM D 422-63 ASTM D 854-83
Moisture content	Gravimetric	NA	Moisture content	PNL-MA-567-SA-7
Matric potential	Filter paper suction	NA	Matric Dotential	PNL-MA-567-SA-10
Bulk density	Gravimetric/volume	NA	Bulk density	PNL-MA-567-SA-8
Moisture retention	Bulk sediment	NA	Moisture retention	ASTM D 2325-68
Saturated hydraulic conductivity	Bulk sediment	NA	Saturated hydraulic conductivity	ASTM D 18.21 (draft in review) Methods of Soil Analysis, Part 2; 13-3.2 and 13-3.3
Anions	Water extract	Methods of Soil Analysis, Part 2; 62-1.3.2.2	IC ISE	PNL-ALO-212 US EPA Method 300.0A Orion-720a
Metals	Water extract Acid leach Fusion	Method of Soil Analysis, Part 2; 62-1.3.2.2 PNL-ALO-106 PNL-ALO-235	ICPMS	PNL-ALO-211
Cation exchange capacity	Bulk sediment	NA	Cation exchange capacity	Methods of Soil Analysis Part 2; 9-3.1

A.4.0 INSTALLATION OF NEW BOREHOLE AT TANK SX-115

A new borehole labeled 299-W23-19 (well number B8809) was installed at tank SX-115. The following activities were conducted at the new borehole.

- Measured formation and casing temperature in the open borehole face after the casing was advanced and after cleaning the borehole during drilling for future correlation analysis.
- Conducted borehole geophysical surveying and analysis (moisture, neutron, gross gamma, spectral gamma and enhanced neutron spectral gamma analysis) for stratigraphic correlation and selected contaminant distribution.
- Performed spectral gamma logging and evaluated the potential use of microspheres to support attempt to determine the occurrence of dragdown during drilling.
- Obtained sediment samples to analyze for the presence and concentration of contaminants and to evaluate alterations of the sediments from waste chemistry effects.
- Obtained sediment samples to support preparation of the borehole geologic logs and stratigraphic and lithologic contact correlation with other boreholes in the WMA S-SX vicinity.

A.4.1 NEW BOREHOLE LOCATION

A new vertical borehole was drilled southwest of tank SX-115 within the SX tank farm. The location of the borehole is 3 m (10 ft) south of drywell 41-15-09 at coordinates Northing 134166.72 and Easting 566759.19, as is shown in Figure A.3. The boring extends from the surface to just below the water table, approximately 64 m (210 ft) bgs, to allow for groundwater sampling.

A.4.2 DRILLING AND SEDIMENT SAMPLING METHODS AND INTERVALS

The new borehole was advanced in conjunction with split-spoon sampling techniques through regions of interest with samples acquired in advance of the conductor casing installation. Then, the boring was cleaned out (i.e., drilled to expand the borehole diameter to approximately the drill pipe and conductor casing diameter while the conductor casing was being driven downward to the bottom of the last sample interval). The reverse-air circulation drill and drive method was used for this task because of the ease of drilling through gravels, cobbles, and boulders common to the area geology. Also, the quantity of drilling residuals (cuttings) is minimal with this technique, washout zones are significantly reduced or eliminated, and more representative formation and water samples can be obtained (Driscoll 1986) compared to previously used methods.

Figure A.3. Tank SX-115 Borehole Sampling Location

Air used in the drilling process had to be contained per the Washington State Department of Health. A Notice of Construction permit (DOE-RL 1999a) were acquired before drilling operations inside the tank farm. The drilling method complies with the requirements of the Washington State Department of Health for the Notice of Construction permit and other pertinent requirements and appropriate engineering systems to prevent the potentially contaminated air from being released to the environment.

Drilling was conducted using specifications and guidance in accordance with WAC 173-160. All waste was handled in accordance with the requirements of "Dangerous Waste Regulations" (WAC 173-303). The drilling and sampling techniques are based on minimizing the exposure of field personnel to both radiation and chemical pollutants, which is the application of as low as reasonably achievable principles in compliance with regulatory requirements.

The new borehole was completed as a RCRA-compliant groundwater monitoring well after completion of the geophysical surveying. All temporary steel casing removed from the boring was surveyed and either decontaminated and released or transferred to an appropriate disposal facility. A 4-in. stainless steel casing and screen was permanently installed, and a flush mount surface protection/well seal was constructed. The well was completed in accordance with WAC 173-160 requirements to meet groundwater protection goals. Specific work steps for well completion were documented in the tank farm work package.

Borehole sampling was performed to define the depth of contamination. The borehole serves to establish the general lithology of the sediments lying below the site and to give indications of how radionuclides and other contaminants have migrated. It also provides sediment samples for determination of sediment chemistry and vadose zone properties.

There is some question as to the geographical extent of the effect of the Hanford Site operations on sediment quality. There are uncertainties as to the extent of the effect of the site activities; therefore, a background sample (i.e., above the base of the tank) was obtained from the drilling of the borehole at SX tank farm. As with all samples, this sample was field screened using alpha, beta, gross gamma, and spectral gamma scans. The results from this sample were evaluated and compared to data from onsite borings to determine whether there has been any significant impact on the sediment below WMA S-SX from the Hanford Site operations. Because the background sample was taken 9 m (30 ft) bgs, any surface contamination present in the drilling location is not expected to have altered the constituent results.

For the new borehole, split-spoon drive sampling began at 3 m (10 ft) bgs to allow for a limited open borehole and placement of a sealed surface casing to prevent air contamination from occurring. Drilling and sampling continued until groundwater was reached. Figure A.4 shows the sampling strategy for the new borehole. The boring extends to just below the water table to permit installation of the Kabis sampler for groundwater sampling in accordance with guidance from the Hanford Groundwater Program (Stewart 1997).

Figure A.4. New Borehole Sampling Strategy

A.4.3 BOREHOLE GEOPHYSICAL SURVEYING ACTIVITIES

Downhole spectral gamma or gross gamma geophysical logging was conducted to ascertain the gamma-emitting radionuclide concentrations and assess contaminant drag-down during advancement of the casing. The spectral gamma or gross gamma logging frequency was directed by CHG. The planning basis for spectral gamma or gross gamma logging frequency included logging every 6.1 to 9.2 m (20 to 30 ft) that the borehole was advanced. If the radiological screening performed by the site health physics technician indicated a zone of high contamination was penetrated, a log was to be run within 4.6 m (15 ft) of passing through that zone.

A full suite of geophysical logs was run any time the casing size was changed and at the completion of the borehole. This provided some flexibility and provided for logging on average every 2 days following Waste Management Northwest's planning basis of advancing the hole 3 m (10 ft) per day.

The following logging techniques were used for the new borehole:

- Gross gamma logging to support correlation of confining layers and stratigraphy
- Spectral gamma logging for measuring the distribution of selected radionuclides
- Neutron log for measuring the degree of saturation distribution
- Neutron-enhanced spectral gamma logging for correlation of high-salt tank waste and moisture content with spectral gamma and neutron probes, respectively
- Infrared temperature gauge for measuring sediment temperature.

The existing equipment and procedures for gross gamma and spectral gamma logging in use at the Hanford Site provide acceptable data (DOE-GJO 1995).

The borehole was decommissioned following completion of the groundwater sampling described in Section A.3.4. All steel casing was removed and transferred to an appropriate disposal facility or controlled decontamination facility, and each boring was pressure-grouted from the bottom up, using a Portland cement/bentonite slurry. The procedures comply with U.S. Environmental Protection Agency requirements and WAC 173-160.

A.4.4 GROUNDWATER SAMPLING ACTIVITIES

The sampling and analyses of groundwater was conducted by the Hanford Groundwater Program as described in Johnson and Chou (1999). The new borehole penetrated the groundwater table; therefore, samples of groundwater were collected and analyzed in accordance with guidance provided in the sampling plan for borehole 41-09-39 (Stewart 1997).

A.4.5 LABORATORY ANALYSIS

The following sections describe the laboratory analyses required for the samples collected from the new borehole. Samples for laboratory analysis were placed in appropriate containers and

properly preserved. All samples for laboratory analysis were transported under chain of custody in accordance with Henderson (1999).

Sediment Sample Analysis

After the split-spoon sediment samples and drill cutting samples were screened, these samples were transported to the Pacific Northwest National Laboratory (PNNL) Applied Geology and Geochemistry group for analysis. All material removed from the borehole was sent to the laboratory for possible future analysis. Samples are contained in airtight sample containers after their initial screening by the health physics technician and are kept under refrigeration. This process is used to retain sediment moisture in as close to field condition as possible. All samples were transported to the laboratory under refrigeration to further limit alteration of sediment moisture.

Sediment subsamples for laboratory analysis were defined by location in the sample after the field screening and geologic logging were completed and indication of contamination locations were identified. Approximately 22 sediment subsamples from the borehole were chosen for screening analysis. The following criteria were used to identify subsamples for laboratory analysis based on concurrence with Ecology.

- One background subsample taken at 9 m (30 ft) bgs.
- One subsample taken at 17 m (55 ft) bgs, at the level of the tank bottom.
- Two subsamples taken at the major lithology changes in the Hanford formation.
- One subsample taken at the Plio-Pleistocene unit and Hanford formation contact, and one subsample obtained at the Ringold Formation and Plio-Pleistocene unit contact.
- One subsample taken just above the water table in the capillary fringe zone.
- One subsample taken at the historic high water table at approximately 56 m (185 ft) bgs.
- Subsamples taken of any paleosols seen in the split-spoon drive samples.
- Subsamples taken in locations where elevated or altered gamma surveying or moisture content was measured during the geological and geophysical borehole logging process.
- At least one subsample taken every 3 m (10 ft) if samples have not already been taken, based on the above criteria to ensure continuous distribution and lithologic completeness.

Figure A.5 shows the subsamples identified for laboratory analyses. All subsamples underwent screening analyses, which consist of nitrate analysis by the colorimetric method, pH measurement, electrical conductance measurement, and gamma energy analysis. These analyses, along with the gamma surveying and moisture content measurements performed during the field geophysical surveys and the laboratory geologic logging, were used to determine the extent of further subsample analysis. Table A.3 identifies the full complement of analyses and their respective laboratory preparation and analytical methods. This paragraph and the remainder of

this section identifies which analyses were conducted on which subsample. If more than one preparation or analytical method is listed, the laboratory geochemistry staff determined which methods would produce the best results and provide the best understanding of the chemistry involved. For those methods that produce multiple constituents (i.e., inductively coupled plasma or volatile organic analysis), all constituents identified were reported. Regulatory hold times were met where appropriate.

Because the purpose of the new borehole analysis is to both gain an understanding of the nature and extent of contamination, the fate and transport of the contaminants in the vadose zone, and to produce RCRA-compliant data, the analysis of these subsamples consisted of two levels. The baseline level involved analysis of organic, inorganic, and radiochemical constituents in full conformance with *Hanford Analytical Services Quality Assurance Requirements Document* (DOE-RL 1998) and with no modifications to methods (as defined in DOE-RL 1998) without concurrence from the CHG technical representative and from Ecology. Substitutions and deviations to methods as defined in DOE-RL (1998) did not require concurrence from Ecology. The second level involved a research-type approach to the analyses. In this level, procedures could be modified or developed to gain a more comprehensive understanding of the dynamics involved. Although specific quality control criteria did not apply to this level, compliance with the other quality assurance requirements of DOE-RL (1998) still had to be met and research analysis had to be initiated only following review and approval of the activities by the CHG technical representative.

The background subsample, backfill – Hanford formation contact subsample, the two subsamples obtained at the Hanford formation and Plio-Pleistocene unit contact and the Plio-Pleistocene unit and Ringold Formation contact, and the subsample obtained just above the water table in the capillary fringe zone were analyzed for the constituents and properties identified in Table A.3. It was recognized before analysis that conditions could occur in which all of the analyses identified in Table A.3 are not warranted (e.g., limited potential for data). These occurrences were to be evaluated on a case-by-case basis. See Appendix B for discussion of what did occur.

The remaining subsamples were analyzed for specific constituents listed in Table A.3 depending on the results of the nitrate, electrical conductivity, and pH screening analyses. A review of the screening analyses results with technical representatives along with Ecology was conducted prior to performing additional analyses. Screening analysis may have been used to determine whether alternative analytical techniques with lower detection limits should be used for specific radionuclides of concern. The screening criteria and associated analytical requirements are identified as follows:

Figure A.5. Tank SX-115 Borehole Subsample Analyses Strategy

**Table A.3. Constituents and Methods for New Borehole Sediment Sample
and Borehole 41-09-39 Decommissioning Sample Analyses (2 Sheets)**

Analysis/ Constituent	Preparation Method	Preparation Procedure Number	Analytical Method	Analytical Procedure Number^a
Cesium-137	Bulk sediment	NA	GEA	PNL-RRL-001
Carbon-14	Bulk sediment Water extract	NA Methods of Soil Analysis, Part 2; 62-1.3.2.2	Total combustion LSC method in review based on:	ASTM D 4129-82 PNL-ALO-476
Europium-152	Bulk sediment	NA	GEA	PNL-RRL-001
Neptunium-237 Plutonium-239 Plutonium-240 Americium-241	Acid leach Fusion	PNL-ALO-106 PNL-ALO-235	ICP-MS	PNLALO-211
Strontium-90	Acid leach Fusion	PNL-ALO-106 PNL-ALO-235	LSC	PNL-ALO-476
Cobalt-60	Bulk sediment	NA	GEA	PNL-RRL-001
Technetium-99	Acid leach Fusion	PNL-ALO-106 PNL-ALO-235	ICP-MS LSC	PNL-ALO-211 PNL-ALO-476
Hydrogen-3	Water extract	Methods of Soil Analysis, Part 2; 62-1.3.2.2	LSC	PNL-ALO-476
Iodine-129	Acidleach	PNL-ALO-106	ICP-MS	PNL-ALO-211
Selenium-79	b	b	b	b
Total uranium	Water extract Fusion	Methods of Soil Analysis, Part 2: 62-1.3.2.2 PNL-ALO-235	ICP-MS	PNL-ALO-211
Metals	Water extract Acid leach Fusion	Methods of Soil Analysis, Part 2; 62-1.3.2.2 PNL-ALO-106 PNL-ALO-235	ICP-MS	PNL-ALO-211
VOA	Bulk sediment		GC/MS	SW846-8260
SVOAs with TICs	Bulk sediment		CG/MS	SW846-8270
pH	Water extract	Methods of Soil Analysis, Part 2; 62-1.3.2.2	Electrometric	Methods of Soil Analysis; 60-3.4
Anions	Water extract	Methods of Soil Analysis, Part 2; 62-1.3.2.2	IC ISE Colorimetric	PNL-ALO-212 US EPA Method 300.0A Orion-720a Hach procedure
Cation exchange capacity	Bulk sediment	NA	Cation exchange capacity	Methods of Soil Analysis Part 2; 9-3.1

**Table 3. Constituents and Methods for New Borehole Sediment Sample
and Borehole 41-09-39 Decommissioning Sample Analyses (2 Sheets)**

Analysis/ Constituent	Preparation Method	Preparation Procedure Number	Analytical Method	Analytical Procedure Number'
Particle size distribution	Bulk sediment	NA	Particle size distribution	ASTM D 422-63 ASTM D 854-83
Mineralogy	Bulk powder/clay	JEA-2, Rev. 0	XRD/SEM/TEM	JEA-3, Rev. 0
Electrical conductance	Water extract	Methods of Soil Analysis, Part 2; 62-1.3.2.2	Electrometric	PNL-MA-567-FA-2
Moisture content	Gravimetric	NA	Moisture content	PNL-MA-567-SA-7
Distribution coefficient	Bulk sediment	NA	Methods for determining radionuclide retardation factors, 1980	PNL-3349 USC-70
Bulk density	Gravimetric/volume	NA	Bulk density	PNL-MA-567-SA-8
Moisture retention	Bulk sediment	NA	Moisture retention	ASTM D 2325-68
Saturated hydraulic conductivity	Bulk sediment	NA	Saturated hydraulic conductivity	ASTMD18.21 (draft in review) Methods of Soil Analysis, Part 2; 13-3.2 and 13-3.3

^aThe procedures are addressed in EPA (1983), EPA (1986), and ASTM (1998).

^bProcedures for analysis of selenium-79 are being prepared; this analysis does not apply to the new borehole.

^cPreparation/extraction procedures for VOA and SVOA analysis will depend on the types of organic compounds present in the sediment.

GEA = gamma energy analysis.

IC = ion chromatography.

ISE = ion selective electrode.

LSC = liquid scintillation.

NA = not applicable.

SEM = scanning electron microscopy.

SVOA = semi-volatile organic analysis.

TEM = transmission electron microscopy.

TIC = tentatively identified compound.

TOC = total organic carbon.

VOA = volatile organic analysis.

XRD = x-ray diffraction.

- Gamma-emitting radioisotopes by gamma energy analysis
- Carbon-14
- Metals and radioisotopes by inductively coupled plasma mass spectrometry
- Tritium and strontium-90 by the liquid scintillation method
- Particle size distribution
- Volatile and semi-volatile organic analysis, including tentatively identified compounds.

A minimum of two subsamples collected within the Hanford formation were to be analyzed for volatile and semi-volatile organic compounds, including tentatively identified compounds and metals.

The data obtained from the above analyses were used to evaluate the location of contamination plumes in the sediment column. If isolated peaks or unusual results were found, additional subsamples from the archived drive sample may have been obtained and analyzed. The results of the above analyses were also used to determine if additional analyses are warranted.

Additional analyses were performed based on the judgement and expertise of the responsible PNNL geochemist, with concurrence from the CHG technical representative and Ecology.

The following analyses were considered for additional analyses:

- Cation exchange capacity
- Mineralogy
- Matric potential
- Distribution coefficient
- Bulk density
- Moisture retention
- Saturated hydraulic conductivity.

Table A.3 identifies the analyses and laboratory methods used for the sample analyses. For the chemical and radiological constituents, the preferred methods are those listed in *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (EPA 1986) or the American Society for Testing and Materials standards (ASTM 1998). The requested constituents may have been analyzed by laboratory-specific procedures, provided that the procedures were validated and conform to DOE-RL (1998). Appendix B discusses the laboratory-specific procedures used. Both the EPA (1986) methods and the PNNL methods listed in Table A.3 are based on techniques from "Methods of Soil Analysis" (ASTM 1998). Therefore, these procedures should be comparable.

A.5.0 INSTALLATION OF SLANT BOREHOLE AT TANK SX-108

The following activities were conducted during installation of a slant borehole at tank SX-108.

- Conduct borehole geophysical surveying and analysis (moisture, neutron, gross gamma, spectral gamma and neutron-enhanced spectral gamma analysis).
- Obtain sediment samples to analyze for the presence and concentration of contaminants and to evaluate alterations of the sediments from waste chemistry effects.
- Obtain sediment samples to support preparation of the borehole geologic logs and stratigraphic and lithologic contact correlation with other boreholes/wells in the WMA S-SX vicinity.

A.5.1 SLANT BOREHOLE LOCATION

The slant borehole is located northwest of tank SX-108 extending under tank SX-108 within the SX tank farm. The location of the borehole is shown in Figure A.6.

A.5.2 DRILLING AND SEDIMENT SAMPLING METHODS AND INTERVALS

One of the primary constraints on sample collection from the 'hot' zone under tank SX-108 was the potential radiation level (greater than 500 mrem/h), which may have limited the sample volumes that could be brought to the surface. To reduce the uncertainties associated with placing a slant borehole beneath tank SX-108, a demonstration was conducted outside of the tank farms to evaluate the techniques for installing the borehole and collecting samples. This demonstration helped refine the borehole angle and the sample collection methods. The planning basis for the SX-108 slant borehole included the following.

- The borehole enters the ground at approximately the 11 o'clock position 12.2 m (40 ft) from the edge of the tank nominally 30° off vertical, heading directly underneath the center of the tank (toward the 5 o'clock position). A preliminary investigation of surface and subsurface interference identified this as a potentially viable location. The borehole depth was to be limited to the Plio-Pleistocene unit or to the maximum depth of contamination, whichever is greater.
- Driven samples were collected ahead of the casing. The samples were transported to the laboratory and analyzed for the contaminants of concern identified in Table A.4. Nominally, 10 horizons would be sampled based on the geophysical surveys or the need to provide depth coverage.

Figure A.6. Tank SX-108 Soil Sampling Location

Table A.4. Constituents and Methods for SX-108 Slant Borehole Sediment Sample Analyses and Near-Surface Characterization Samples (4 Sheets)

Contaminants of Potential Concern	CAS #	Action Levels		Name/Analytical Technology ^a	Target Required Quantitation Limits				Precision Water (%)	Accuracy Water (%)	Precision Soil (%)	Accuracy Soil (%)
		RR ^b (pCi/g)	Cf ^c (pCi/g)		Water ^b Low Level (pCi/L)	Water ^b High Level (pCi/L)	Soil Other Low Level (pCi/g)	Soil Other High Level (pCi/g)				
Radionuclide												
Americium-241	14596-10-2	3.10E+01	2.10E+02	Americium isotopic - AEA	1	400	1	4,000	+20	70-130	+35	70-130
Carbon-14	14702-75-5	5.20E+00	3.31E+04	Carbon-14 - liquid scintillation	200		50	NA	+20	70-130	+35	70-130
Cesium-137	10045-97-3	6.20E+00	2.50E+01	Gamma energy analysis	15	200	0.1	2,000	+20	70-130	+35	70-130
Cobalt-60	10198-40-0	1.40E+00	5.20E+00	Gamma energy analysis	35	200	0.05	2,000	+20	70-130	+35	70-130
Europium-153	14683-23-9	3.30E+00	1.20E+01	Gamma energy analysis	50	300	0.1	2,000	+20	70-130	+35	70-130
Europium-154	15585-10-1	3.00E+00	1.10E+01	Gamma energy analysis	50	200	0.1	2,000	+20	70-130	+35	70-130
Europium-155	14391-16-3	1.25E+02	4.49E+02	Gamma energy analysis	50	300	0.1	2,000	+20	70-130	+35	70-130
Neptunium-237	13994-20-2	2.50E+00	6.22E+01	Neptunium-237 - AEA	1		1	8,000	+20	70-130	+35	70-130
Nickel-63	13981-37-8	4.03E+03	3.01E+06	Nickel-63 - liquid scintillation	15	NA	50	NA	+20	70-130	+35	70-130
Plutonium-238	13981-16-3	3.74E+01	4.73E+01	Plutonium isotopic - AEA	1	130	1	1,300	+20	70-130	+35	70-130
Plutonium-239/240	PCU-239/240	3.39E+01	4.37E+02	Plutonium isotopic - AEA	1	130	1	1,300	+20	70-130	+35	70-130
Total radioactive strontium or strontium-90	SR-RAD or 10098-97-2	4.50E+00	2.50E+03	Total radioactive strontium or strontium isotopic - QPC	2	30	1	800	+20	70-130	+35	70-130
Technetium-99	14133-76-7	5.70E+00	4.10E+05	Technetium-99 - liquid scintillation	15	400	15	4,000	+20	70-130	+35	70-130
Thorium-232	TH-232	1.00E+00	5.10E+00	Thorium isotopic - AEA (pCi)	1	0.002 mg/L	1	0.02 mg/Kg	+20	70-130	+35	70-130
Uranium-234	13966-29-5	1.60E+02	1.20E+03	Uranium isotopic - AEA (pCi)	1	0.002 mg/L	1	0.02 mg/Kg	+20	70-130	+35	70-130
Uranium-235	15117-96-1	2.60E+01	1.00E+02	Uranium isotopic - AEA (pCi)	1	0.002 mg/L	1	0.02 mg/Kg	+20	70-130	+35	70-130
Uranium-238	U-238	8.40E+01	4.20E+02	Uranium isotopic - AEA (pCi)	1	0.002 mg/L	1	0.02 mg/Kg	+20	70-130	+35	70-130

Description of action levels in Table A.1.cdr

Table A.4. Constituents and Methods for Slant Borehole Sediment Sample Analyses and Near-Surface Characterization Samples (4 Sheets)

Contaminants of Potential Concern	CAS #	Action Levels	Name/Analytical Technology ^a	Target Required Quantitation Limits				Precision Water (%)	Accuracy Water (%)	Precision Soil (%)	Accuracy Soil (%)
				Water ^b Low Level (ug/L)	Water ^b High Level (ug/L)	Soil Other Low Level (ug/Kg)	Soil Other High Level (ug/Kg)				
PCBs	1336-36-3	5.00E+02	6.50E+04	0.5	5	16.5	100	e	e	e	e
Cyanide	57-12-5	2.00E+04	2.00E+04	5	5	500	500	e	e	e	e
Lead	7439-92-1	3.53E+05	3.53E+05	100	200	10,000	20,000	e	e	e	e
Lead	7439-92-1	3.53E+05	3.53E+05	10	NA	1,000	NA	e	e	e	e
Mercury	7439-97-6	N/A	N/A	0.5	5	NA	NA	e	e	e	e
Mercury	7439-97-6	3.30E+02	3.30E+02	N/A	N/A	200	200	e	e	e	e
Nickel	7440-02-0	3.30E+04	7.00E+04	40	40	4,000	4,000	e	e	e	e
Silver	7440-22-4	8.00E+03	1.00E+04	20	30	3,000	2,000	e	e	e	e
Silver	7440-22-4	8.00E+03	1.00E+04	5	NA	500	NA	e	e	e	e
Antimony	7440-36-0	3.30E+04	1.40E+06	60	120	6,000	12,000	e	e	e	e
Antimony	7440-36-0	3.30E+04	1.40E+06	10	NA	1,000	NA	e	e	e	e
Arsenic	7440-38-2	6.50E+03	6.50E+03	100	200	10,000	20,000	e	e	e	e
Arsenic	7440-38-2	6.50E+03	6.50E+03	10	NA	1,000	NA	e	e	e	e
Barium	7440-39-3	1.32E+05	2.45E+05	200	200	20,000	20,000	e	e	e	e
Barium	7440-39-3	1.32E+05	2.45E+05	5	NA	500	NA	e	e	e	e
Beryllium	7440-41-7	1.51E+03	1.51E+03	5	10	500	1,000	e	e	e	e
Cadmium	7440-43-9	5.00E+02	5.00E+02	5	10	500	1,000	e	e	e	e
Cadmium	7440-43-9	5.00E+02	5.00E+02	5	NA	500	NA	e	e	e	e
Chromium (total)	7440-47-3	1.60E+06	3.50E+06	10	10	1,000	2,000	e	e	e	e
Chromium (total)	7440-47-3	1.60E+06	3.50E+06	10	NA	1,000	NA	e	e	e	e
Chromium VI	18540-29-9	3.00E+03	1.75E+04	10	4,000	500	200,000	e	e	e	e
Copper	7440-50-8	5.92E+04	1.30E+05	25	25	2,500	2,500	e	e	e	e
Selenium	7782-49-2	5.00E+03	5.00E+03	100	200	10,000	20,000	e	e	e	e
Selenium	7782-49-2	5.00E+03	5.00E+03	10	NA	1,000	NA	e	e	e	e
Uranium (total)	7440-61-1	2.40E+05	1.05E+07	0.1	20	1,000	200	+20	70-130	+35	70-130

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Table A.4. Constituents and Methods for Slant Borehole Sediment Sample Analyses and Near-Surface Characterization Samples (4 Sheets)

Constituents of Potential Concern	CAS #	Action Levels		Name/Analytical Technology ^a	Target Required Quantitation Limits				Precision Water (%)	Accuracy Water (%)	Precision Soil (%)	Accuracy Soil (%)
		Method B (ug/Kg)	Method C (ug/Kg)		Water ^b Low Level (ug/L)	Water ^b High Level (ug/L)	Soil Other Low Level (ug/Kg)	Soil Other High Level (ug/Kg)				
Ammonia-ammonium	7664-41-7	2.72E+07	5.95E+07	Ammonia - 350 N ^d	50	300,000	500	3,000,000	e	e	e	e
Phosphate	14265-44-2	N/A	N/A	Anions - 9056 - IC	500	15,000	5,000	40,000	e	e	e	e
Nitrate	14797-55-8	4.40E+06	4.40E+06	Anions - 9056 - IC	250	10,000	2,500	40,000	e	e	e	e
Nitrite	14797-65-0	3.30E+05	3.30E+05	Anions - 9056 - IC	250	15,000	2,500	20,000	e	e	e	e
Nitrate/nitrite as N	NO3 ⁻ NO2 ⁻ N	3.30E+05	3.30E+05	Nitrate/nitrite - 353 N ^d	75	N/A	750 ^c	N/A	e	e	e	e
Sulfate	14808-79-8	2.50E+07	2.50E+07	Anions - 9056 - IC	500	15,000	5,000	40,000	e	e	e	e
Chloride	16837-40-6	2.50E+07	2.50E+07	Anions - 9056 - IC	200	5,000	2,000	5,000	e	e	e	e
Fluoride	16984-48-8	9.60E+04	3.00E+05	Anions - 9056 - IC	500	5,000	5,000	5,000	e	e	e	e
Sulfides	18494-35-8	N/A	N/A	Sulfide - 9030 - colorimetric	500	N/A	5,000	N/A	e	e	e	e
Bromide	24959-67-9	N/A	N/A	Anions - 9056 - IC	250	N/A	2,500	N/A	e	e	e	e
pH		N/A	N/A	pH - 9045 - electrode	N/A	N/A	N/A	N/A	e	e	e	e
Total organic carbon/total carbon	TOC/TC	N/A	N/A	ASTM D4139-82 - total combustion/colorimetric	1 ppm	1 ppm	1 ppm	1 ppm	e	e	e	e
Cation exchange capacity	CEC	N/A	N/A	Cation exchange capacity/Methods of Soil Analysis Part 2.9-3.1	N/A	N/A	N/A	N/A	f	f	f	f
Particle size distribution	N/A	N/A	N/A	ASTM D 422-63, ASTM D 854-83	N/A	N/A	N/A	N/A	f	f	f	f
Mineralogy	N/A	N/A	N/A	XRD/SEM/TEM/IEA-3, Rev. 0	N/A	N/A	N/A	N/A	f	f	f	f
Electrical conductance	EC	N/A	N/A	Electrometric/	N/A	N/A	N/A	N/A	f	f	f	f
Moisture content	N/A	N/A	N/A	PML-MA-567-SA-2	N/A	N/A	N/A	N/A	f	f	f	f
Moisture potential	N/A	N/A	N/A	Moisture content/	N/A	N/A	N/A	N/A	f	f	f	f
Matric potential	N/A	N/A	N/A	PML-MA-567-SA-7	N/A	N/A	N/A	N/A	f	f	f	f
Distribution coefficient	K _d	N/A	N/A	Methods for determining radionuclide retardation factors. 1980/PNL-3349 USC-70	N/A	N/A	N/A	N/A	f	f	f	f
Bulk density	N/A	N/A	N/A	Bulk density/	N/A	N/A	N/A	N/A	f	f	f	f

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Table A.4. Constituents and Methods for Slant Borehole Sediment Sample Analyses and Near-Surface Characterization Samples (4 Sheets)

Contaminants of Potential Concern	CAS #	Action Levels		Name/Analytical Technology ^a	Target Required Quantitation Limits				Precision Water (%)	Accuracy Water (%)	Precision Soil (%)	Accuracy Soil (%)
		Method B (ug/Kg)	Method C (ug/Kg)		Water ^b Low Level (ug/L)	Water ^b High Level (ug/L)	Soil Other Low Level (ug/Kg)	Soil Other High Level (ug/Kg)				
Moisture retention	Q ^c	N/A	N/A	Moisture retention/ ASTM D 2325-68	N/A	N/A	N/A	N/A	f	f	f	f
Saturated hydraulic conductivity	K _s	N/A	N/A	Saturated hydraulic conductivity/ASTM D18.21 (draft in review) Methods of Soil Analysis, Part 2, 13-3.2 and 13-3.3	N/A	N/A	N/A	N/A	f	f	f	f

Note: For the chemical and radiological constituents the preferred methods are those listed in *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (EPA 1986) or *Standard Test Methods for Materials* (ASTM 1998).

^aWater values for sampling quality control (e.g. equipment blanks/runs) or drainable liquid (if recovered).

^bAll four digit numbers refer to *Test Methods for Evaluating Solid Waste* (EPA 1986).

^cValues from *Hanford Guidance for Radiological Cleanup* (WDOH 1997). Italicized values are calculated using the same parameters as the WDOH guidance.

^dMethods for Chemical Analysis of Water and Wastes (EPA 1983).

Precision and accuracy requirements as identified and defined in the referenced U.S. Environmental Protection Agency procedures.

Precision and accuracy for these measurements are not required because of the nature of the measurement.

AEA = alpha energy analysis.

ASTM = American Society for Testing and Materials.

CI = commercial industrial.

CAS = chemical abstracts service.

CVAA = cold vapor atomic absorption.

GC = gas chromatography.

GFC = gas proportional counting.

IC = ion chromatography.

ICP = inductively coupled plasma.

ICPMS = inductively coupled plasma mass spectrometry.

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N/A = not applicable.

NA = not available.

PCB = polychlorinated biphenyl.

ppm = parts per million.

PR = rural residential.

SEM = scanning electron microscopy.

TEM = transmission electron microscopy.

TOC/TC = total organic carbon/total carbon.

WDOH = Washington Department of Health.

XRD = x-ray diffraction.

Appropriate permits and compliance with the Notice of Construction permit (DOE-RL 1999a) were maintained during the drilling operations for inside the tank farm. The selected drilling method complies with the requirements of the Washington State department of Health for the Notice of Construction permit and other pertinent requirements and appropriate engineering systems to prevent the possible contaminated air from being released to the environment.

Drilling was conducted using specifications and guidance in accordance with WAC 173-160. The technique for collecting sediment samples was a removable tip in conjunction with a split-spoon sampler that allowed driven samples to be collected ahead of the casing. The removable tip concept may have led to contamination problems on the inside of the borehole casing and required the tip to be replaced with a new one each time it was removed and limited the ability to geophysical log the borehole. The split-spoon sampler that used was approximately 5 cm (2 in.) in diameter by 0.6 m (2 ft) long with a 10 cm (4 in.) diameter shielded lead casing around the sampler. The hole was 10 cm (4 in.) in diameter after the sample was collected, but only a 5 cm (2 in.) sample was collected and brought to the surface. The 0.6 m (2 ft) sample allowed for the depth of penetration to be beyond potential disturbed sediments below the end of the hole and brought sediments unable to be handled to the surface. This approach was demonstrated outside the tank farms prior to implementation inside the tank farms. This method collected enough sediment sample to be analyzed and provided the least amount of disturbance, therefore providing a sample that was as close as possible to being a representative sample.

There are backup approaches that could have been taken to collect sediment samples during casing extraction if collecting a split-spoon sample was found to be impractical. These options include using a sidewall sampling tool and scraping or under-reaming the hole and collecting the material with a split-spoon sampler. These backup approaches were not needed.

Contaminant dragdown during drilling and sampling activities is unavoidable and has been observed in recent sampling activities. Different drilling/sampling techniques impact dragdown to varying degrees. Because the objective of the characterization activities identified in the DQO is to safely sample in and below the 'hot' zone in a region of known leakage and not to tag the leading edge of a contaminant plume, the dragdown issue was a secondary concern.

The depth of the vadose zone boring was to the maximum depth of contamination.

Sediment Sampling Activities

For the SX-108 slant borehole, sediment sampling was conducted beginning at 16.7 m (55 ft) bgs and continued at discrete intervals of approximately 1.5 m (5 ft) until maximum depth of contamination or the Plio-Pleistocene unit was reached. Figures A.7 and A.8 show the slant borehole location and sampling strategy.

After the sediment samples were screened, these samples were transported to the PNNL Applied Geology and Geochemistry group for analysis. All material removed from the borehole was sent to the laboratory for possible future analysis. Samples were contained in airtight sample containers after their initial screening by the health physics technician and kept under refrigeration. This process is used to retain sediment moisture in as close to field condition as possible. All samples were transported to the laboratory under refrigeration to further limit alteration of sediment moisture.

Figure A.7. Tank SX-108 Slant Borehole

Figure A.8. Tank SX-108 Slant Borehole Subsample Analyses Strategy

Waste containing unknown, low-level mixed radioactive waste and/or hazardous waste contained, stored, and disposed of according with Appendix D of *Phase I RCRA Facility Investigation/Corrective Measures Study WorkPlan for Single-Shell Tank Waste Management Areas* (DOE-RL 1999b) and specified in the quality assurance project plan (Appendix A of DOE-RL 1999b) and is documented in the field activity reports. Waste was disposed of in accordance with Appendix D of DOE-RL (1999b) and the waste acceptance criteria for the Mixed Waste Burial Grounds. All important information was recorded on field activity report forms per approved procedures. A field activity report form includes borehole number, site location drawings, drawing of the downhole tool strings, site personnel, sampling types and intervals, zones noted by the health physics technician as elevated in radiological contaminants, instrument readings and the depth represented by those readings, and specific information concerning borehole completion.

The SX-108 slant borehole was abandoned following completion of the geophysical surveying. All steel casing was removed and transferred to an appropriate disposal facility or controlled decontamination facility. The borehole was pressure-grouted from the bottom up, using a Portland cement/bentonite slurry or other appropriate material in accordance with WAC 173-160. Specific procedures for borehole abandonment were documented in the field work package. These procedures comply with U.S. Environmental Protection Agency requirements and WAC 173-160.

A.5.3 BOREHOLE GEOPHYSICAL SURVEYING

Based on sampling and construction methods, downhole spectral gamma or gross gamma geophysical logging was conducted to ascertain the gamma-emitting radionuclide concentrations. The spectral gamma or gross gamma logging frequency was directed by CHG.

A full suite of geophysical logs was run any time the casing size was changed and at the completion of the borehole. Because the sampling method involves pulling split-spoon samples up through the borehole, there was a high probability that the inner bore of the casing would become contaminated. Following completion of the sampling, the contamination levels were evaluated and a determination was made on the utility of geophysically logging the borehole.

The following logging techniques may have been used for the slant borehole:

- Gross gamma logging to support correlation of confining layers and stratigraphy
- Spectral gamma logging for measuring the distribution of selected radionuclides
- Neutron log for measuring the relative moisture content
- Neutron-enhanced spectral gamma logging for correlation of high-salt tank waste and moisture content with spectral gamma and neutron probes, respectively.

The existing equipment and procedures for gross gamma and spectral gamma logging in use at the Hanford Site provide acceptable data (DOE-GJO 1995).

A.5.4 GROUNDWATER SAMPLING AND ANALYSIS

No sampling of groundwater was conducted for the SX-108 slant borehole characterization effort.

A.5.5 LABORATORY ANALYSES OF SX-108 SLANT BOREHOLE

Sediment Sample Analysis

Geologic logging for the SX-108 slant borehole was conducted as it was for the borehole 41-09-39 extension. Specifically, once sample material from the slant borehole was received at the laboratory, it was geologically logged by an assigned geologist in general conformance with standard procedures. The assigned geologist photographed the samples and described the geologic structure, texture, and lithology of the recovered samples. Special attention was paid to the presence of contaminant alteration. If such a phenomenon were noted, that sample was noted; preserved for more detailed physical, chemical, and mineralogic analyses; and recorded in the laboratory notebook.

Sediment samples for laboratory analysis were defined by location in the sample after the field screening and geologic logging were completed, and indication of contamination locations were identified. Approximately 10 sediment samples from the borehole were chosen for screening analysis. Screening analyses consisted of the following:

- Nitrate
- Electrical conductivity
- Total organic carbon
- pH.

The following criteria were used to identify samples for laboratory analysis based on concurrence with Ecology.

- One subsample was taken at approximately 17 m (55 ft) bgs, at or near the base of the tank.
- Subsamples were taken at the major lithology changes in the Hanford formation.
- One subsample was taken at the Plio-Pleistocene unit and Hanford formation contact.
- Subsamples were taken in locations where elevated or altered gamma surveying was measured during the geological and geophysical borehole logging process based on nearby geophysical drywell logging.
- At least one subsample was taken every 3 m (10 ft) if samples were not already taken, based on the above criteria to ensure continuous distribution and lithologic completeness.

Worker safety considerations have limited the collection of samples at certain intervals. Figure A.8 shows the subsamples identified for laboratory analyses. A 1:1 water extract of all subsamples underwent screening analyses, which consist of nitrate analysis by the colorimetric

method, pH measurement, and electrical conductance measurement. In addition each subsample was directly measured for gamma emitters by gamma energy analysis. These analyses, along with the gamma surveying and moisture content measurements performed during the field geophysical surveys and the geologic logging, were used to determine the extent of further subsample analysis. Table A.4 identifies the full complement of analyses and their respective laboratory preparation and analytical methods. This paragraph and the remainder of this section identify which analysis was conducted on which sample. If more than one preparation or analytical method is listed, the laboratory geochemistry staff determined which methods would produce the best results and provide the best understanding of the chemistry involved. For those methods that produce multiple constituents (i.e., inductively coupled plasma), all constituents identified were reported. Every effort was made to meet regulatory holding times where appropriate.

Because the purpose of the slant borehole analysis was to gain an understanding of the nature and extent of contamination, the fate and transport of the contaminants in the vadose zone, and to produce RCRA-compliant data, the analysis of these subsamples consisted of two levels. The baseline level involved analysis of inorganic and radiochemical constituents in full conformance with DOE-RL (1998) and with no modifications to methods (as defined in DOE-RL 1998) without concurrence from the CHG technical representative and from Ecology. Substitutions and deviations to methods as defined by DOE-RL (1998) did not require concurrence from Ecology. The second level involved a research-type approach to the analyses. In this level, procedures may have been modified or developed to gain a more comprehensive understanding of the dynamics involved. Although specific quality control criteria do not apply to this level, compliance with an approved quality assurance plan provided by the primary laboratory was performed and research analysis was initiated following notification and approval of the activities by the CHG technical representative.

The backfill – Hanford formation contact sample, peak gamma concentration sample, and the sample obtained at the Hanford formation and Plio-Pleistocene unit contact were analyzed for the constituents and properties identified in Table A.4. It was recognized that conditions could occur when all of the analyses identified in Table A.4 were not warranted (e.g., limited potential for data). These occurrences were evaluated on a case-by-case basis.

One sample from at or near the base of the tank was analyzed for volatile organics identified in Table A.5.

**Table A.5. Constituents and Methods for Organic Analysis
of Borehole Sediment Samples**

Analysis/Constituent	Preparation Method	Preparation Procedure Number	Analytical Method	Analytical Procedure Number
VOA	Bulk Sediment		GCMS	SW846-8260
SVOAs with TICS	Bulk sediment		GC/MS	SW846-8270
PCBs ^b	Bulk Sediment		GC	GW846-8082

^a Preparation/extraction procedures for VOA and SVOA analysis will depend on the types of organic compounds present in the sediment.

^b Analyzed on selected samples collected from the near-surface characterization effort.

GC = gas chromatography.

MS = mass spectrometry.

PCB = polychlorinated biphenyl.

SVOA = semi-volatile organic analysis.

TIC = tentatively identified compounds.

VOA = volatile organic analysis.

The remaining samples were analyzed for specific constituents listed in Table A.4 depending on the results of the nitrate, electrical conductivity, total organic carbon, total carbon, and pH screening analyses. A review of the screening analyses results with technical representatives and Ecology was conducted prior to performing additional analyses. Screening analysis may have been used to determine whether alternative analytical techniques with lower detection limits were to be used for specific radionuclides of concern. The screening criteria and associated analytical requirements were identified as follows:

- Gamma-emitting radioisotopes by gamma energy analysis
- Metals and radioisotopes by inductively coupled plasma-mass spectrometry
- Tritium and strontium-90 by the liquid scintillation method
- Particle size distribution
- Carbon 14.

A minimum of two samples collected within the Hanford formation were analyzed for metals as identified in Table A.4.

The data obtained from the above analyses were used to evaluate the location of contamination plumes in the sediment column. The results of the above analyses were also used to determine if additional analyses are warranted. Additional analyses were performed based on the judgement and expertise of the responsible PNNL geochemist, with concurrence from the CHG technical representative and Ecology. The following analyses were performed as additional analyses:

- Cation exchange capacity
- Mineralogy
- Matric potential
- Distribution coefficient
- Bulk density

- Moisture retention
- Saturated hydraulic conductivity.

Tables A.4 and A.5 identify the analyses and laboratory methods used for the sample analyses. For the chemical and radiological constituents, the preferred methods are those listed in EPA (1986) or American Society for Testing and Materials standards (ASTM 1998). The requested constituents may have been analyzed by laboratory-specific procedures, provided that the procedures were validated and conform to DOE-RL (1998). Both the EPA (1986) methods and the PNNL methods listed in Tables A.4 and A.5 are based on techniques from "Methods of Soil Analysis" (ASTM 1998). Therefore, these procedures should be comparable. The detection limit, precision, and accuracy guidelines for the parameters of interest are listed in the DQO workbook for WMA S-SX (Ovink 1999).

A.6.0 NEAR-SURFACE CHARACTERIZATION

The following sections describe the near-surface characterization conducted in the S tank farm. These activities involved deployment of a truck-mounted, direct-push vehicle to collect the data.

A.6.1 LOCATION

Two areas have been identified as regions of interest for the Phase 1 characterization of the shallow vadose zone soil. These areas are within the north end of the S tank farm. The S tank farm areas of interest include:

- Unplanned release near diversion box 241-S-B
- East of tank S-104 near the fence (in the drainage path of the unplanned release that occurred in the SY tank farm and flowed into the S tank farm).

A.6.2 INVESTIGATIVE AND SAMPLING METHODS AND INTERVALS

For the purpose of the DQO, the shallow investigation of 2 areas comprised collecting samples between the tank farm surface and approximately 16.7 m (55 ft) bgs using direct-push technology at 9 locations within either or both of these 2 areas (Figure A.9).

Shallow soil characterization was carried out using a truck-mounted cone penetrometer-based system. Specific sites cleared for access (underground piping and electrical services identified) and with an approved excavation permit were interrogated with a gross gamma/spectral gamma cone penetrometer probe. The depth of investigation was determined by the depth to which the probe could be advanced using a standard deployment truck. The probe was deployed using the gross gamma mode with the tool advanced at approximately 2 cm/sec (0.8 in./sec). If in the upper 5 m (15 ft) the downhole instrument indicated a potential cesium-137 concentration of 3.7 pCi/g or greater, logging was shifted to the spectral mode to determine the presence and level of concentration of cesium-137; below 5 m (15 ft) the threshold limit for spectral gamma determinations was 20 pCi/g. In zones where cesium-137 is present at concentrations greater than 20 pCi/g, spectral gamma readings were taken at 0.5 m (1.5 ft) intervals. In all cases, gross gamma measurements were to be taken while the probe was advanced.

The graphical log developed using the gross and spectral gamma measurements was used to select intervals to be sampled. The sampling push was made in a location no more than 0.7 m (2 ft) from the site of the gamma push. A single point sampler will be used to collect the required samples. Sampling intervals were selected from those horizons with a cesium-137 concentration of 20 pCi/g or greater. In the event that horizons were penetrated that would yield samples having a greater than 50 mrem/h dose rate at 30 cm (12 in.) (based on calculations using sampler size and cesium-137 concentration), a sample was collected from the first interval below the high rate zone having a dose rate of less than 50 mrem/h.

Two separate areas were characterized the vicinity of tank S-102 and the vicinity of tank S-104. These two sites exhibit separate instances of cesium-137 in vadose zone drywells that may be indicative of near-surface sources. In addition, the region to the east of tank S-104 has potentially been impacted by a tank overfill event in the 241-SY double-shell tank farm. A total of nine push sites were identified. An average of four samples per site were collected.

Figure A.9. Waste Management Area S-SX Shallow Soil Sampling Locations

A.6.2.1 Tank S-104 Site

The highest recorded levels of cesium-137 contamination associated with the tank S-104 site are in borehole 40-04-05 in the southeast quadrant of the tank. Contamination was estimated at about 10^6 pCi/g at a depth of about 14 m (48 ft) bgs. Up to five sets of gamma probe and sampling pushes were conducted to investigate this site. The pushes included the following.

- Adjacent to the 40-04-05 drywell, between the drywell and the tank. This location was to ascertain if there is a vertical gradient between the push location and the identified elevation of contamination in 40-04-05 and to collect a sample from below the contaminated zone to determine if mobile contaminants are moving ahead of the cesium-137 hot spot.
- Adjacent to tank S-104 at the 5 o'clock position. This location was as close to the tank as the push-truck could be positioned within dome-load restrictions. The S tank farm tanks are constructed with a spare inlet port at this point. Experience in other farms has shown that these spare inlet ports are subject to failure if a tank is overfilled. This push tested the hypothesis that the contamination adjacent to the tank is due to an overfill event.
- Adjacent to the normal fill line at the 3 o'clock position. This location was within 3 to 4.5 m (10 to 15 ft) of the tank and as close to the fill line as safety considerations allow. This location was used to determine the horizontal and vertical extent of the contamination found in the 40-04-05 borehole.
- Adjacent to the S tank farm fence. This location was used to determine the impact to shallow soils due to the surface release and subsequent ponding that occurred in the SY tank farm.
- Midway between the previous two pushes. This location was only to be interrogated if positive determinations of contamination were found in one of the two previous pushes.

A.6.2.2 Tank S-102 Site

The highest recorded levels of cesium-137 contamination associated with the 241-S-102 site are in borehole 40-02-03 in the northeast quadrant of the tank. Contamination was estimated at about 10^6 pCi/g at a depth of about 6 m (20 ft) bgs. Four sets of gamma probe and sampling pushes were conducted to investigate this site. The pushes included the following.

- Adjacent to tank S-102, northwest of drywell 40-02-03. Because no contamination is detected in drywell 40-02-01, this push was used to determine the extent of contamination in a northwesterly direction from borehole 40-02-03. The push was situated about midway between the boreholes and as near the tank as safety considerations allow.
- Along the line projected between 40-02-01 and 40-02-03, north of the cascade line between tanks S-101 and S-102. This location provided information on the extent of contamination known to exist at 40-02-03 and assess the depth of movement of that contamination.

- Along the line projected between 40-02-01 and 40-02-03, south of the cascade line between tanks S-101 and S-102, and near the 241-S-A diversion box. This location provided information as to the extent and general direction of movement of contaminants for this site. In addition, the accumulation pit associated with the 241-S-A was assessed as a possible contributor to the contamination.
- Adjacent to the 241-S-B diversion box. The potential for contamination in this region related to operation of the 241-S-B accumulation pit was assessed.

A.6.2.3 Additional Pushes

Additional pushes have been made based on the information developed during the initial campaign or decisions of the River Protection Project Vadose Zone Project management. These additional pushes were determined based on the determined extent of contamination and (1) the availability of both the push truck and crew and (2) availability of budget and support personnel.

Any samples were transported to the laboratory and analyzed for the contaminants of concern identified in Table A.4. A detailed field work plan was prepared to identify the number and location of samples to be collected.

A.6.3 GEOPHYSICAL SURVEYING ACTIVITIES

Prior to sediment sampling using the direct push, downhole gross gamma and spectral gamma geophysical surveying was conducted to ascertain the gamma-emitting radionuclide concentration in the surrounding sediments. After each push with the direct-push or each borehole with the hollow-stem auger, decommissioning occurred.

A.6.4 LABORATORY ANALYSES

Laboratory analyses included radiological and chemical analyses of selected sediment samples. Physical and hydrologic analyses of selected sediment samples was performed.

Once received at the laboratory, these samples underwent analysis using the analytical methods listed in Table A.4. These analyses are sample-limited. Therefore, hold points were inserted into the process to allow the laboratory and CHG technical staff to collaborate and review data before each new round of analyses. Analyses were reprioritized based on the results of other measurements. See Appendix B for discussion of the analyses conducted.

Based on the results of the screening analyses identified in the SX-108 slant borehole, spectral gamma surveys performed during the field geophysical surveys, and the geologic logging and field notes, geological technical experts, CHG technical staff, the laboratory technical staff, and decision makers (Ecology and the U.S. Department of Energy) convened to determine what, if any, additional analyses were to be conducted. Some of the determining criteria were the amount and integrity of the remaining sample, screening analytical results, and regulatory requirements. Based on these decisions, additional analyses were performed.

A.7.0 REFERENCES

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APPENDIX B

RESULTS FROM WORK PLAN ACTIVITIES

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LIST OF TERMS

bgs	below ground surface
PPlc	lower Plio-Pleistocene
PPlz	upper Plio-Pleistocene
RCRA	<i>Resource Conservation and Recovery Act of 1976</i>
S&T	Science and Technology
WMA	waste management area

B.1.0 INTRODUCTION

Several field characterization studies were completed to increase understanding of the vadose zone contamination as it presently exists in waste management area (WMA) S-SX. The results of those studies are summarized in this appendix. The primary information obtained from those activities was that resulting from extensive analyses of soil samples taken from several boreholes in the WMA (Figure B.1). Those boreholes were as follows.

- Borehole **41-09-39** – Lies southwest of tank SX-108 and was extended from 40 m (130 ft) below ground surface (bgs) to groundwater. This borehole was extended to further characterize soil contamination caused by a *tank* SX-108 leak. It was extended from the depth it was drilled to support a previous characterization effort to determine the extent of tank fluid migration in that location and to determine groundwater impacts. Further discussion of borehole 41-09-39 soil sampling and analyses is provided in Section B.2.0.
- Borehole **299-W23-19** – Lies just southwest of tank SX-115. This borehole **was** drilled from the surface to groundwater to further characterize vadose zone contamination caused by a SX-115 leak and to determine groundwater impacts from the leak. Further discussion of borehole 299-W23-19 soil sampling and analyses is provided in Section B.3.0.
- Tank **SX-108** Slant Borehole – A slanted hole was driven underneath tank SX-108. This borehole was drilled into the Plio-Pleistocene unit to characterize soils **as** near to the source of the tank SX-108 leak **as** possible and to investigate contaminant behavior underneath that *tank*. Further discussion of borehole SX-108 soil sampling and analyses is provided in Section B.4.0.
- Boreholes **299-W22-48 and 299-W22-50** – Borehole 299-W22-48, located east of S tank farm, and borehole 299-W22-50, located southeast of SX *tank* farm, are *Resource Conservation and Recovery Act of 1976* (RCRA) groundwater monitoring wells. These boreholes are close enough to the tank farms to be considered representative of *tank* farm vadose zone soils. Because the soils have not come into contact with tank fluids, their characteristics provide a means of defining tank farm vadose zone soil characteristics prior to tank leaks. Further discussion of boreholes 299-W22-48 and 299-W22-50 soil sampling and analyses is provided in Section B.5.0.

The characterization information summarized in this appendix includes brief descriptions of borehole geology, geophysical logs, moisture contents, soil suction data, soil water chemistry, and groundwater contamination data, if appropriate. In the interest of brevity, data reported here are those which have the most direct bearing on potential contaminant characteristics and migration. More background information is available in the referenced documents (Seme et al. 2001a,b,c,d).

In addition to the boreholes drilled and characterization of borehole samples, a shallow soils cone penetrometer study was completed around tank S-104 in the S *tank* farm to characterize near-surface contamination in that area. Further discussion of that study is provided in Section B.6.0.

Figure B.1. Locations of Boreholes Sampled in Waste Management Area S-SX Characterization Studies

B.2.0 BOREHOLE 41-09-39 CHARACTERIZATION

This section summarizes data reported in *Geologic and Geochemical Data Collected from Vadose Zone Sediments from Borehole SX 41-09-39 in the S/SX Waste Management Area and Preliminary Interpretations* (Serne et al. 2001b) except for the groundwater sample data which are reported in *RCRA Groundwater Quality Assessment Report for Waste Management Area S-SX (November 1997 through April 2000)* (Johnson and Chou 2001). Borehole 41-09-39 was completed to further characterize the nature and extent of vadose zone contamination from the tank SX-108 leak. The data reported here are a follow-on from a previous drilling and sampling program (Myers et al. 1998) in which the borehole was drilled down to 40 m (130 ft) bgs. In the recent study the borehole was extended to groundwater, and soil samples were taken and analyzed from 40 m (130 ft) bgs to 68.6 m (225 ft) bgs. Also, sidewall coring samples were collected between 8 and 40 m (25 and 130 ft) bgs as the borehole was being decommissioned. Extensive analyses of these sediment samples were also completed. The method used to advance and sample this borehole may have contributed to cross-contamination of portions of each sample interval. Core was taken to recognize and minimize the impact of these occurrences for this field investigation report.

The most significant data provided by this characterization effort were measurements on sediment samples for radionuclides and chemicals attributed to the tank SX-108 leak. Elevated concentrations of several constituents were primarily measured in soils between 19 and 40 m (61 and 130 ft) bgs. This depth interval includes the Hanford formation H1 and H2 subunits. The primary radionuclides present in this zone are cesium-137 and technetium-99. Maximum cesium-137 concentrations are present in subunit H1 between 20 and 25 m (65 and 83 ft) and at lesser amounts in subunit H2 between 25 and 30 m (83 and 108 ft). The presence of **high** levels of cesium-137 at borehole 41-09-39 is indicative of strong lateral movement of tank fluid and attributed to unusually high cesium-137 mobility shortly after release from tank SX-108. Maximum technetium-99 concentrations are present in the subunit H2 between 24 and 39 m (79 and 129 ft). The primary chemical characteristics attributed to tank fluid-soil interaction within this zone are elevated pH, sodium, chromium, and nitrate. The depth of maximum technetium-99 concentration coincides with high nitrate concentrations and marks the leading edge of vertical tank fluid migration in the direction measurable in this borehole.

The measured moisture contents are somewhat **dry** relative to undisturbed Hanford formation soils. Soil suction measurements suggest that drainage is occurring in the soil column but the measured soil suction variability is too high to quantify rate of drainage. The lack of tank fluid contaminants below the Plio-Pleistocene unit and the low concentrations of technetium-99, and nitrate in groundwater samples from borehole 41-09-39 supports the hypothesis that contaminants from this area may not have reached the unconfined aquifer.

B.2.1 GEOLOGY AT BOREHOLE 41-09-39

Borehole 41-09-39 was originally installed to a depth of 39.8 m (130.5 ft) bgs in December 1996. The borehole was installed by advancing a thick-walled casing with a sealed, hardened drive point using a pile driver. No samples could be collected or analyzed due to the nature of this original construction. Subsequently, the drive point was milled-off and the borehole deepened to groundwater. A cable-tool drilling rig was used to deepen and collect

samples to **68.6 m (225 ft)** bgs. Split-spoon samples were collected whenever possible. Borehole decommissioning was subsequently completed in **1999** by grouting the void space to eliminate a potential preferential pathway for contaminant migration. During decommissioning of this borehole, side-wall sediment samples were collected from preselected horizons in the upper, previously unsampled portion of the bore. The nature of the side-wall sampler precluded collection of any coarse grained materials during decommissioning.

B.2.1.1 Hanford formation

No Hanford formation samples were collected during the original construction of borehole **41-09-39**. In addition, the sediment samples collected using the side-wall sampler during decommissioning were unsuitable for geologic interpretation. Samples that were collected were biased toward fine-grained materials due to the nature of the sampling device.

B.2.1.2 Plio-Pleistocene Unit

The top of the Plio-Pleistocene unit is not identified in this borehole. The first samples collected during the extension were from the upper Plio-Pleistocene (PPlz) subunit. The lower Plio-Pleistocene (PPlc) subunit was also present.

- **Subunit PPlz** – Subunit PPlz is interpreted to be present from the start of sampling at **39.8 m (130.5 ft)** bgs to about **47.5 m (155.8 ft)** bgs. The upper sampled sediments consist of a very fine-grained sequence that is a thin-bedded, up to **0.3 m (1 ft)** thick, silty very fine-grained sand to silt. The graded silty sand to silt beds appear to become thicker and more massive with depth. Beds in the middle portion of the sequence are on the order of **1 m (3 ft)** thick and about **1.5 m (5 ft)** thick at the bottom. The sand ranges from moist to dry and friable. Some silt stringers up to **1 cm (0.4 in.)** thick were observed. Two massively bedded silt to clayey silt units are present; one from **43.5 to 44.2 m (142.8 to 144.9 ft)** bgs and a second from **46 to 47.3 m (151 to 155 ft)** bgs. The upper unit is described as moist with a strong to weak reaction to hydrogen chloride. It is a massively bedded clayey silt to silt at the base, grading upward to a silty sand, then back to a silt at the top. The lower silt to clayey silt layer is described as very compacted. Some small stratifications of very fine-grained sand with limonitic staining are present. The base of the PPlz subunit is dominated by a well-sorted **20 cm (8 in.)** thick fine sand.
- **Subunit PPlc** – Subunit PPlc is approximately **1.3 m (4.3 ft)** thick extending to approximately **48.6 m (160 ft)** bgs. This horizon ranges in grain size from sandy silt to sandy gravel. It is moderately to strongly cemented with pinkish to whitish calcium carbonate. In places the calcium carbonate cement is massive, forming a calcrete layer that was broken up during drilling. In other places the calcium carbonate appears disseminated into the sand or silt matrix or as coatings on the gravel clasts.

B.2.1.3 Ringold Formation

The Ringold Formation consists predominately of weakly cemented sandy gravel to strongly cemented matrix-supported conglomerate and is correlated with the member of Wooded Island unit E.

The gravel-conglomeritic facies is both clast supported and matrix supported. The matrix ranges from a sandy mud to muddy fine sand to well-sorted quartz-rich fine or medium sand to very

coarse sand. Gravel clasts are subrounded to rounded and range up to 70 mm (2.8 in.). The clasts are predominately composed of quartzite, basalt, and granite. In places the basalt and granitic clasts are highly weathered and limonitic staining is common.

Intercalated sand and silt-mud lenses are common. These minor strata range in thickness from a few centimeters to nearly 1 m (3 ft). The sand units range from silty fine to very fine sand to clean, well-sorted fine or medium **quartz** sand to poorly sorted, gravelly, muddy, coarse- to fine-grained sand.

Silty and muddy units are generally poorly sorted and consist of slightly gravelly sandy silt to gravelly mud. Two thin (6 to 24 cm [2 to 9 in]), clean mud units were observed at 61.6 m (202.2 ft) bgs and 63.3 m (207.5 ft) bgs.

B.2.2 GEOPHYSICAL AND PHYSICAL PROPERTY MEASUREMENTS AT BOREHOLE 41-09-39

Downhole geophysical measurements at borehole 41-09-39 included a cadmium zinc tellurium gross gamma log and a drilling resistance log down to 40 m (130 ft) bgs, high-purity germanium spectral gamma logs from 40 m (130 ft) bgs to groundwater (about 65 m [214 ft] bgs), and neutron-neutron logs over the entire depth. Geophysical data for between 8 and 40 m (25 and 130 ft) bgs and between 40 and 65 m (130 and 214 ft) bgs are shown in Figures B.2 and B.3, respectively. The geophysical data provide features that distinguish stratigraphic units in the vadose zone. Subunit H1 shows a high gross gamma count because of the high cesium-137 content and a high drilling resistance because of the high gravel content. The Plio-Pleistocene unit shows relatively high natural thorium-232 and uranium-238 levels and moisture content.

Laboratory measurements of soil moisture content (Table B.1 and Figure B.4) show similar trends in relative concentrations as the neutron-neutron moisture measurements. Matric potential values were also measured (Figure B.5). While the majority of the data are indicative of a draining profile, a number of measurements suggest upward flow. Seme et al. (2000b) attributes this to the drying effect resulting from the head loading imposed by the contents of tank SX-108. The data variability is not indicative of unit gradient conditions nor does it provide any indication of deep drainage.

B.2.3 SOIL WATER CHEMISTRY MEASUREMENTS

In addition to soil physical property measurements (Section B.2.2), an extensive water chemistry analysis has been completed for borehole 41-09-39 samples collected between 8 and 65 m (25 and 215 ft) bgs. The primary means of measuring porewater composition was to add deionized water to soil samples to generate enough water for performing analyses. By back-calculating for the dilution introduced by the added water, 'true' concentrations were derived. For a few samples porewater was directly separated from the same soil sample or one nearby and analyzed directly. By comparing the dilution-corrected water extract data with the porewater data in these few samples, an indication of the closeness of the water extract chemistry to original water chemistry was determined. In general, comparisons were not exact but concentration values were generally within a factor of two or better, agreement improved with increasing constituent concentration, and both sets of data showed similar concentrations versus soil depth correlations. Thus, the water extract method is an effective tool for evaluating tank fluid interactions with vadose zone soil.

Figure B.2. Gamma-Ray, Drilling Resistance, and Moisture Logs
for the Upper Portion of Borehole 41-09-39

Source: MACTEC-ERS 1997.

**Table B.1. Moisture Content (wt%) of Borehole 41-09-39
Sidewall Cores and Extension Sleeves (2 Sheets)**

Depth (ft bgs)	Sample ID	Moisture Content (%)	Depth (ft bgs)	Sample ID	Moisture Content (%)	Depth (ft bgs)	Sample ID	Moisture Content (%)
Sidewall			149.9	8B	9.7	183.9	36C	3.37
25.5	15A/B/C	8.12	151.1	9C	12.8	184.6	36B	2.06
44.5	14A/B/C	8.57	151.8	9B	NM	185.8	37D	1.39
56.5	13A/B/C	16.27	152.8	9A	13.9	186.2	37c	2.6
61.5	12A/B/C	12.84	153.4	10C	13.6	186.8	37B	2.35
65.5	11A/B	4.71	153.9	10B	14.7	187.2	37A	2.09
66	11C	5.29	154.5	10A	19.6	187.8	38C	2.87
69.5	10A/B/C	4.36	155.1	11D	5.4	188.3	38B	1.9
74.5	9A/B/C	5.17	155.4	11C	4.3	188.7	38A	1.8
79.5	8A/B/C	10.71	155.9	11B	3.5	189.2	39B	1.54
82.5	7A/B/C	8.41	156.4	11A	4.5	189.5	39A	1.93
		10.25	156.8	12B	6.9	190.7	40A	5.13
			157.1	12A	6.6	193.3	45A	5.28
102.5	5A/B/C *		157.2	13D	6.4	195.9	47D	8.84
108.5	4A/B/C	12.01	157.7	13C	4	196.4	47C	6.62
112	2B/C	8.17	158.2	13B	5.3	196.9	47B	5.74
127.4	1A/B/C	12.66	159.4	14C	5.9	197.4	47A	4.94
Extension			160	14B	5.8	199.1	49B	8.25
131.1	1C	NM	160.6	14A	7.6	199.1	49A	9.53
131.7	1B	13	162.3	16D	13.3	199.4	50B	6.83
133.2	2D	35.6	162.8	16C	13.5	199.4	50A	3.89
133.7	2 c	18.3	163.3	16B	4.1	200.2	52B	5.47
133.7	2C-2	26.1	163.8	16A	4.4	200.7	52A	8.15
134.2	2B	14.5	164.3	17D	4.91	202.5	54B	6.58
134.7	2A	16	164.8	17C	3.56	202.5	54A	5.44
135.9	3A	13.1	165.3	17B	5.27	204.3	56C	7.74
137.4	4C	10.9	165.8	17A	4.91	205	56B	6.58
138	4B	11.7	166.6	18C	9.7	205.6	56A	5.44
138.7	4A	16.1	167.1	18B	4.7	207.6	58D	9.4
139.9	5D	14.1	167.7	18A	4.7	208.1	58C	10.18
140.3	5 c	14.5	169.9	20A	4.3	208.6	58B	10.57

**Table B.1: Moisture Content (wt%) of Borehole 41-09-39
Sidewall Cores and Extension Sleeves (2 Sheets)**

Depth (ft bgs)	Sample ID	Moisture Content (%)	Depth (ft bgs)	Sample ID	Moisture Content (%)	Depth (ft bgs)	Sample ID	Moisture Content (%)
140.9	5B	12.6	171.3	22C	5.8	209	58A	8.16
141.5	5A	9.4	172	22B	5.2	209.4	59D	10.1
141.9	6F	11	178.2	28A	7.94	209.8	59c	12.49
142.4	6E	9.6	178.8	30C	6.9	210.4	59B	17.5
143.3	6D	21.8	179.2	30B	3.35	210.9	59A	24.97
144.1	6C	26	179.7	30A	3.11	211.7	62B	8.15
144.7	6B	22.9	180.2	31B	4.36	212.1	62A	10.03
145.2	7E	8.7	180.5	31A	3.72	212.9	64B	12.58
145.8	7D	9.5	181.1	32B	5.31	213.3	64A	13.19
146.4	7C	11.2	181.5	32A	3.15	214.1	65B	7.76
146.4	7C-R	11.2	183	35B	3.56	214.3	65A	8.6
148.3	8C	7.4	183.3	35A	2.84			

* One of the three cores may be different depth at 5A/B/C.

NM = not measured.

Figure B.4. Moisture Content (wt%) versus Depth for Vadose Sediments from Borehole 41-09-39

Figure B.5. Soil Suction Profile for Samples Taken from Borehole 41-09-39

Water extract pH and electrical conductivity measurements with depth are listed in Table B.2 and graphed in Figure B.6. Elevated pH values (8.5 to 9.7) are measured between 20 and 25 m (65 and 83 ft) bgs primarily in subunit H1 of the Hanford formation. Because pH values are expected to decrease as increasing interaction with soil and soil water occurs, the location of maximum pH values suggests the approximate initial depth of tank fluid interaction with the vadose zone at this location. Increases in electrical conductivity values compared to undisturbed soil water values are also an indicator of tank fluid occurrence in soil. Substantive increases are measured between 20 and 40 m (65 and 132 ft) bgs with maximum values (approximately 98,000 to 524,000 $\mu\text{S}/\text{cm}$) between 25 and 39 m (83 and 127 ft) bgs, primarily in subunit H2. Maximum electrical conductivity values are an indicator of location for mobile tank fluid constituents and maximum vertical penetration of tank fluids along the pathway sampled at this location.

Water extract anion concentrations as a function of depth are listed in Table B.3. Nitrate, chloride, and sulfate concentrations with depth are shown in Figure B.7. The primary indicator of tank fluid occurrence is elevated nitrate concentrations which is measured in this borehole between 20 and 41 m (65 and 136 ft) bgs with maximum values between 25 and 39 m (83 and 127 ft) bgs. Elevated levels of chloride (between 25 and 39 m [83 and 127 ft] bgs) and sulfate (between [20 and 39 m [65 and 127 ft] bgs) are also observed. Chloride maximum concentrations (between 27 and 34 m [90 and 112 ft] bgs) track closely with nitrate in subunit H2. An isolated chloride peak occurs at 60 m (197 ft) bgs, which may be a residual from groundwater present when the water table was elevated and has since drained. The sulfate peak occurs between 25 and 34 m (83 and 112 ft) bgs. The sulfate peak occurs between 25 and 34 m (83 and 112 ft) bgs, a maximum concentration depth interval that also coincides with chloride and nitrate. Also, sulfate shows a slight increase in concentration at 56 and 58 m (185 and 189 ft) bgs where the isolated chloride peak occurred in the Ringold Formation. Between 56 and 58 m (185 and 189 ft) bgs represents the high groundwater elevation.

Water extract cation concentrations as a function of depth are listed in Table B.4 and graphed in Figure B.8. Among the cations, elevated sodium concentrations are the primary tank fluid indicator. Maximum values begin abruptly at 25 m (83 ft) bgs and remain elevated above 10,000 mg/L until 34 m (112 ft) bgs. Calcium, magnesium, potassium, and natural strontium show depleted concentrations at 19 to 24 m (61 to 80 ft) bgs and above the high sodium zone and show elevated concentrations between 27 and 39 m (90 and 127 ft) bgs, a depth range coincident and perhaps slightly ahead of the high sodium range. The relative positioning of sodium concentration ranges versus that of the other cations supports the hypothesis that sodium preferentially replaces these cations in sorption sites as it migrates vertically and pushes them ahead to the leading edge of a leak plume.

The last group of constituents analyzed included radionuclides and trace metals. Of these, cesium-137, technetium-99, and chromium (Tables B.5 and B.6) are clearly present in concentrations above background and are attributed to have originated in the tank fluid. Water extract concentrations of cesium-137 are listed in Table B.5 and distribution is shown in Figure B.9. Above-background cesium-137 concentrations are measured between 8 and 42 m (25 and 137 ft) bgs.

**Table B.2. Measurements of pH and Electrical Conductivity for 1:1 Water Extracts of
Borehole 41-09-39 Sidewall and Extension Sleeves (3 Sheets)**

Depth (ft bgs)	Sample ID	1:1 extract pH	1:1 extract ($\mu\text{S}/\text{cm}$)	Corrected ($\mu\text{S}/\text{cm}$)	Depth (ft bgs)	Sample ID	1:1 extract pH	1:1 extract ($\mu\text{S}/\text{cm}$)	Corrected ($\mu\text{S}/\text{cm}$)	Depth (ft bgs)	Sample ID	1:1 extract pH	1:1 extract ($\mu\text{S}/\text{cm}$)	Corrected ($\mu\text{S}/\text{cm}$)
Sidewall														
25.5	15A/B/C	8.39	188	2317	141.9	6F	8.49	255	4886	165.3	17B	7.77	149	2828
44.5	14A/B/C	8.52	226	2638	142.4	6E	8.36	203	4389	165.8	17A	7.78	93.0	2031
56.5	13A/B/C	8.31	287	1790	143.3	6D	8.46	300	3033	166.6	18C	8.10	181	1861
61.5	12A/B/C	8.61	355	2767	144.1	6C	8.29	353	3057	167.1	18B	7.85	99.0	2100
65.5	11A/B	9.18	899	19092	144.7	6B	8.5	314	3036	167.7	18A	7.94	105	2246
66	11C	9.76	504	9535	145.2	7E	8.75	194	2328	169.9	20A	8.35	216	5033
69.5	10A/B/C	9.18	752	17248	145.8	7D	8.7	212	2209	171.3	22C	8.43	250	4295
74.5	9A/B/C	9.60	719	13928	146.4	7C	8.41	237	2097	172.0	22B	8.33	180	3433
79.5	8A/B/C	9.55	1722	16090	148.3	8C	8.71	236	3160	178.2	28A	8.46	231	2897
82.5	7A/B/C	8.70	8293	98684	149.9	8B	8.71	200	2032	178.8	30C	8.36	183	2637
90	6A/B	8.33	41820	408017	152.8	9A	8.91	210	1489	179.2	30B	7.62	67.0	2000
95.5	3A/B/C	7.93	41010	521060	153.4	10C	8.75	277	1997	179.7	30A	7.72	74.0	2375
102.5	5A/B/C	8.01	41910	402855	153.9	10B	8.7	254	2085	180.2	31B	8.42	214	4892
108.5	4A/B/C	8.07	56480	470722	154.5	10A	8.75	221	1085	180.5	31A	8.39	201	5395
112	2B/C	8.12	42770	524413	155.4	11C	8.62	163	3736	181.1	32B	8.51	267	5044
127.4	1A/B/C	7.92	16550	130789	155.9	11B	8.64	155	4431	181.5	32A	8.30	151	4793
Extension														
131.1	1C	8.52	382	N/A	156.4	11A	8.67	114	4788	183.0	35B	8.50	261	7334
131.7	1B	8.06	4858	36192	157.1	12A	8.63	317	4761	183.9	36C	8.18	137	4052
133.2	2D	8.26	865	1817	157.2	13D	8.55	289	4471	184.6	36B	7.85	67.0	3247

**Table B.2. Measurements of pH and Electrical Conductivity for 1:1 Water Extracts of
Borehole 41-09-39 Sidewall and Extension Sleeves (3 Sheets)**

Depth (ft bgs)	Sample ID	1:1 extract pH	1:1 extract ($\mu\text{S/cm}$)	Corrected ($\mu\text{S/cm}$)	Depth (ft bgs)	Sample ID	1:1 extract pH	1:1 extract ($\mu\text{S/cm}$)	Corrected ($\mu\text{S/cm}$)	Depth (ft bgs)	Sample ID	1:1 extract pH	1:1 extract ($\mu\text{S/cm}$)	Corrected ($\mu\text{S/cm}$)
133.7	2C	8.28	413	1648	157.7	13C	8.8	311	7731	185.0	36A	7.96	94.0	5493
134.2	2B	8.36	658	4363	158.2	13B	8.7	190	3576	185.8	37D	7.87	68.0	4891
134.7	2A	8.25	611	3629	158.7	13A	7.21	207	3912	186.2	37C	7.48	49.0	1886
135.2	3B	8.25	831	5618	159.4	14C	8.5	270	4552	186.8	37B	7.66	40.0	1699
135.9	3A	8.34	442	3266	160	14B	8.46	215	3726	187.2	37A	7.57	45.0	2155
137	4D	8.29	387	3150	160.6	14A	8.38	189	2482	187.8	38C	8.16	121	4201
137.4	4C	8.78	172	1538	162.3	16D	8.28	245	1813	188.3	38B	7.75	58.0	3046
138	4B	8.61	223	1846	162.8	16C	8.52	319	2313	188.7	38A	7.35	24.0	1337
138.7	4A	8.63	193	1141	163.3	16B	8.02	117	2828	189.2	39B	7.95	79.0	5131
140.3	5C	8.57	230	1520	163.8	16A	7.79	92	2112	189.5	39A	8.11	123	6379
140.9	5B	8.92	184	1417	164.3	17D	8.36	268	5435	190.7	40A	7.77	59.0	1147
141.5	5A	8.97	167	1737	164.8	17C	8.31	322	9000	193.3	45A	8.79	275	5239
195.9	47D	8.23	93.0	1048										
196.4	47C	8.16	101	1523										
196.9	47B	7.40	71.0	1243										
197.4	47A	7.70	76.0	1546										
198.8	49C	8.22	165	1838										
199.1	49B	8.17	149	1803										
199.1	49A	8.13	152	1605										
199.4	50B	8.22	103	2412										
199.4	50A	7.81	102	2631										

Table B.2. Measurements of pH and Electrical Conductivity for 1:1 Water Extracts of Borehole 41-09-39 Sidewall and Extension Sleeves (3 Sheets)

Depth (ft bgs)	Sample ID	1:1 extract pH	1:1 extract ($\mu\text{S}/\text{cm}$)	Corrected ($\mu\text{S}/\text{c}$)m	Depth (ft bgs)	Sample ID	1:1 extract pH	1:1 extract ($\mu\text{S}/\text{cm}$)	Corrected ($\mu\text{S}/\text{cm}$)	Depth (ft bgs)	Sample ID	1:1 extract pH	1:1 extract ($\mu\text{S}/\text{cm}$)	Corrected ($\mu\text{S}/\text{cm}$)
200.2	52B	8.45	160	2928										
200.7	52A	8.33	148	1814										
202.5	54B	8.08	135	2067										
202.5	54A	7.96	93.0	1721										
204.3	56C	7.94	86.0	1082										
205	56B	8.16	122	1479										
205.6	56A	8.07	94.0	1208										
207.6	58D	8.26	191	2034										
208.1	58C	8.30	160	1576										
208.6	58B	7.87	60.0	569										
209	58A	7.56	42.0	513										
209.4	59D	8.06	103	1017										
209.8	59C	7.72	56.0	452										
210.4	59B	7.72	55.0	316										
210.9	59A	8.80	710.	284										
211.7	62B	7.81	50.0	610										
212.1	62A	7.73	51.0	512										
212.9	64B	8.04	92.0	1122										
213.3	64A	7.99	76.0	762										
214.1	65B	7.85	87.0	1124										
214.3	65A	7.93	72.0	838										

Figure B.6. Concentrations of pH, Electrical Conductivity, and Nitrate in Dilution-Corrected Water Extract

Table B.3. Anion Concentrations at Borehole 41-09-39 in 1:1 Water Extracts (3 Sheets)

Depth (ft bgs)	Sample ID	1:1 Extracts					Dilution Factor	Dilution Ratio Corrected				
		Nitrate (ppm)	Chloride (ppm)	Flu e (p	Nitrite (ppm)	Sulfate (ppm)		Nitrate (ppm)	Chloride (ppm)	Fluoride (ppm)	Nitrite (ppm)	Su ⁺ ate (ppm)
Sidewall												
25.5	15A/B/C	13.0	<0.3	NM	0.26	1.70	12.3	161	<4.0	NM	3.18	20.9
44.5	14A/B/C	13.0	0.92	NM	0.26	16.4	11.7	152	10.7	NM	3.01	191
56.5	13A/B/C	13.0	0.84	NM	0.26	<2.8	6.24	81.0	5.22	NM	1.61	<17.2
61.5	12A/B/C	13.0	0.81	NM	0.26	5.13	7.79	102	6.34	NM	2.01	40.0
65.5	11A/B	29.1	0.52	NM	0.26	11.5	21.2	618	10.9	NM	5.48	244
66.0	11C	17.6	0.26	NM	0.26	6.45	18.9	333	4.89	NM	4.88	122
69.5	10A/B/C	33.5	0.38	NM	0.26	8.66	22.9	767	8.80	NM	5.91	199
74.5	09A/B/C	44.3	0.54	NM	0.26	18.1	19.4	857	10.5	NM	5.00	351
79.5	08A/B/C	371	3.34	NM	1.40	51.7	9.34	3464	31.3	NM	13.1	483
82.5	07A/B/C	2836	30.1	NM	82.1	336	11.9	33746	358	NM	976	3999
90.0	06A/B	28044	307	NM	139	271	9.76	273614	2992	NM	1355	2642
95.5	03A/B/C	32767	321	NM	28.6	260	12.7	416332	4074	NM	364	3308
102.5	05A/B/C	31666	198	NM	133	198	9.61	304385	1903	NM	1279	1904
108.5	04A/B/C	42448	359	NM	130	386	8.33	353773	2990	NM	1084	3215
112.0	02B/C	32764	344	NM	106	373	12.3	401733	4212	NM	1297	4576
127.4	01A/B/C	12808	77.5	NM	28.6	73.3	7.90	101213	613	NM	226	579
Extension												
134.2	2B	291	NM	NM	NM	NM	6.63	1929	NM	NM	NM	NM
134.7	2A	268	NM	NM	NM	NM	5.94	1592	NM	NM	NM	NM
135.2	3B	382	NM	NM	NM	NM	6.76	2447	NM	NM	NM	NM
135.9	3A	165	NM	NM	NM	NM	7.39	1219	NM	NM	NM	NM

Table B.3. Anion Concentrations at Borehole 41-09-39 in 1:1 Water Extracts (3 Sheets)

Depth (ft bgs)	Sample ID	1:1 Extracts				Dilution Factor	Dilution Ratio Corrected					
		Nitrate (ppm)	Chloride (ppm)	Fluoride (ppm)	Nitrite (ppm)		Sulfate (ppm)	Nitrate (ppm)	Chloride (ppm)	Fluoride (ppm)	Nitrite (ppm)	Sulfate (ppm)
Extension (Cont'd)												
137.4	4C	12.0	NM	NM	NM	NM	8.94	107	NM	NM	NM	NM
138	4B	24.0	NM	NM	NM	NM	8.28	199	NM	NM	NM	NM
140.3	5C	9.90	NM	NM	NM	NM	6.61	65.4	NM	NM	NM	NM
140.9	5B	3.70	NM	NM	NM	NM	7.70	28.5	NM	NM	NM	NM
141.5	5A	9.80	NM	NM	NM	NM	10.4	102	NM	NM	NM	NM
141.9	6F	9.10	NM	NM	NM	NM	19.2	174	NM	NM	NM	NM
142.4	6E	14.0	NM	NM	NM	NM	21.6	303	NM	NM	NM	NM
143.3	6D	42.0	NM	NM	NM	NM	10.1	425	NM	NM	NM	NM
144.1	6C	58.0	NM	NM	NM	NM	8.66	502	NM	NM	NM	NM
144.7	6B	48.0	NM	NM	NM	NM	9.67	464	NM	NM	NM	NM
145.2	7E	18.0	NM	NM	NM	NM	12.0	216	NM	NM	NM	NM
145.8	7D	32.0	NM	NM	NM	NM	10.4	333	NM	NM	NM	NM
146.4	7C	36.0	NM	NM	NM	NM	8.85	319	NM	NM	NM	NM
152.8	9A	24.0	NM	NM	NM	NM	7.09	170	NM	NM	NM	NM
153.4	10C	48.0	NM	NM	NM	NM	7.21	346	NM	NM	NM	NM
153.9	10B	49.0	NM	NM	NM	NM	8.21	402	NM	NM	NM	NM
154.5	10A	33.0	NM	NM	NM	NM	4.91	162	NM	NM	NM	NM
155.4	11C	9.80	NM	NM	NM	NM	22.9	225	NM	NM	NM	NM
155.9	11B	8.40	NM	NM	NM	NM	28.6	240	NM	NM	NM	NM
156.4	11A	5.30	NM	NM	NM	NM	42.0	223	NM	NM	NM	NM
156.8	12B	10.5	NM	NM	NM	NM	14.3	151	NM	NM	NM	NM

Table B.3. Anion Concentrations at Borehole 41-09-39 in 1:1 Water Extracts (3 Sheets)

Depth (ft bgs)	Sample ID	1:1 Extracts				Dilution Factor	Dilution Ratio Corrected				
		Nitrate (ppm)	Chloride (ppm)	Fluoride (ppm)	Nitrite (ppm)		Sulfate (ppm)	Nitrate (ppm)	Chloride (ppm)	Fluoride (ppm)	Nitrite (ppm)
Extension (Cont'd)											
157.1	12A	7.50	NM	NM	NM	15.0	112	NM	NM	NM	NM
157.2	13D	2.00	NM	NM	NM	15.5	30.9	NM	NM	NM	NM
157.7	13C	6.20	NM	NM	NM	24.9	154	NM	NM	NM	NM
158.2	13B	6.80	1.00	0.45	<0.06	18.8	128	18.8	8.50	<1.1	273
162.8	16C	1.90	NM	NM	NM	7.25	13.8	NM	NM	NM	NM
163.3	16B	4.60	NM	NM	NM	24.2	111	NM	NM	NM	NM
163.8	16A	6.70	NM	NM	NM	23.0	153	NM	NM	NM	NM
164.8	17C	0.30	NM	NM	NM	28.0	8.4	NM	NM	NM	NM
165.3	17B	7.60	NM	NM	NM	19.0	144	NM	NM	NM	NM
165.8	17A	10.8	NM	NM	NM	21.8	236	NM	NM	NM	NM
172	22B	5.00	3.00	1.40	<0.06	19.1	95.4	57.2	26.7	1.10	248
179.2	30B	4.70	1.30	0.38	<0.04	29.9	140	38.8	11.3	1.20	140
184.6	36B	3.00	1.60	0.52	<0.06	48.5	145	77.5	25.2	<2.9	179
189.2	39B	0.80	2.40	0.56	<0.06	65.0	51.3	155	36.4	<3.9	221
196.9	47B	18.0	110	0.21	<0.06	17.5	315	1926	3.70	<0.5	43.8
200.2	52B	<0.10	3.70	0.81	<0.06	18.3	<1.8	67.7	14.8	<1.1	403
208.6	58B	0.60	1.50	0.48	<0.06	9.49	5.20	14.2	4.6	<0.6	23.7
211.7	62B	0.60	1.00	0.48	<0.06	12.2	7.70	12.2	5.9	<0.7	32.9
214.1	65B	<0.10	1.50	0.45	<0.06	12.9	<1.29	19.4	5.8	<0.8	71.1

Figure B.7. Dilution-Corrected 1:1 Sediment to Water Extract Anions and Actual Porewater Anion Concentrations versus Lithology and Depth

Table B.4. Major Cation Composition of 1:1 Water Extracts from Borehole 41-09-39 Sidewall Cores and Extension Sleeves (3 Sheets)

Depth (ft bgs)	Sample ID	Calcium (ppm)	Potassium (ppm)	Magnesium (ppm)	Sodium (ppm)	Strontium (ppm)	Aluminum (ppm)	Boron (ppm)	Iron (ppm)	Manganese (ppm)	Silicon (ppm)
25.5	15A/B/C	9.30	6.40	1.10	29.5	(0.053)	0.84	5.20	0.51	(0.01)	21.5
44.5	14A/B/C	6.00	6.90	0.70	41.8	(0.049)	0.59	15.9	0.14	(0.01)	14.8
56.5	13A/B/C	22.4	7.40	2.00	43.2	(0.036)	0.51	5.30	<0.25	<0.05	9.30
61.5	12A/B/C	3.60	2.60	0.30	80.7	(0.042)	0.56	31.0	(0.05)	(0.01)	7.50
65.5	11A/B	1.10	(1.70)	0.40	121	(0.035)	1.48	9.00	2.03	(0.04)	14.2
66.0	11C	0.90	2.60	1.90	212	(0.051)	5.72	10.5	8.97	0.13	37.0
69.5	10A/B/C	0.80	3.60	1.00	176	(0.035)	3.08	4.50	4.27	0.08	24.0
74.5	9A/B/C	0.50	(2.40)	(0.10)	168	(0.047)	0.65	10.3	(0.11)	<0.05	12.5
79.5	8A/B/C	0.70	4.20	(0.10)	423	(0.057)	0.75	35.6	(0.02)	<0.05	5.30
82.5	7A/B/C	22.1	16.0	2.20	2041	0.46	(0.48)	16.9	(0.02)	<0.05	7.00
90.0	6A/B	142	209	7.20	11270	2.68	(0.37)	26.6	(0.04)	<0.05	3.00
95.5	3A/B/C	975	129	19.8	10209	15.1	(0.22)	12.4	(0.06)	<0.05	3.60
102.5	5A/B/C	563	128	24.1	10753	10.1	(0.20)	14.0	(0.08)	<0.05	3.70
108.5	4A/B/C	449	117	17.3	15256	8.76	(0.26)	8.30	(0.08)	<0.05	4.80
112.0	2B/C	453	81.2	23.7	11344	8.56	<0.50	30.2	(0.06)	<0.05	4.90
127.4	1A/B/C	1705	76.7	186	1921	13.6	<0.50	15.7	(0.04)	0.10	5.10
134.2	2B	49.3	5.38	12.9	31.3	0.22	<0.05	1.82	<0.05	<0.05	4.60
134.7	2A	57.4	4.29	13.8	22.5	0.26	<0.05	0.45	<0.05	<0.05	6.00
135.2	3B	57.3	22.4	15.0	53.6	0.26	<0.05	1.86	<0.05	0.06	7.90
135.9	3A	39.2	(10.7)	8.18	23.4	0.4	<0.05	0.77	<0.05	0.06	4.20

**Table B.4. Major Cation Composition of 1:1 Water Extracts from
Borehole 41-09-39 Sidewall Cores and Extension Sleeves (3 Sheets)**

Depth (ft bgs)	Sample ID	Extension (Cont'd)									
		Calcium (ppm)	Potassium (ppm)	Magnesium (ppm)	Sodium (ppm)	Strontium (ppm)	Aluminum (ppm)	Boron (ppm)	Iron (ppm)	Manganese (ppm)	Silicon (ppm)
137.4	4C	19.7	(1.60)	3.13	10.8	0.06	<0.05	0.29	<0.05	<0.05	5.00
138.0	4B	20.0	(8.10)	3.98	14.8	0.06	<0.05	0.37	<0.05	<0.05	5.40
140.3	5C	16.0	(3.20)	3.62	19.0	0.06	<0.05	0.50	<0.05	<0.05	6.60
140.9	5B	21.8	(6.60)	3.21	14.2	0.07	<0.05	0.41	<0.05	<0.05	4.70
141.5	5A	17.8	(2.40)	3.24	(13.5)	0.07	<0.05	0.34	<0.05	<0.05	6.30
141.9	6F	19.7	4.07	6.07	19.3	0.09	<0.05	1.45	<0.05	<0.05	9.70
142.4	6E	13.4	4.83	4.18	15.0	0.07	-0.06	0.99	<0.05	<0.05	10.0
143.3	6D	20.3	5.08	7.21	19.9	0.09	<0.05	0.54	<0.05	<0.05	10.7
144.1	6C	25.3	7.24	9.17	25.2	0.13	(0.07)	0.67	<0.05	<0.05	12.3
144.7	6B	22.4	5.15	8.09	22.0	0.1	<0.05	0.72	<0.05	<0.05	11.3
145.2	7E	12.1	(2.50)	3.88	17.5	0.05	(0.08)	1.23	<0.05	<0.05	11.2
145.8	7D	13.1	(2.90)	4.26	18.9	0.06	(0.14)	1.98	<0.05	<0.05	13.5
146.4	7C	15.3	(3.80)	5.53	20.1	0.08	(0.06)	1.26	<0.05	<0.05	14.3
151.1	9C	15.0	5.02	4.94	16.1	0.07	(0.07)	1.29	<0.05	<0.02	9.90
151.8	9B	13.2	4.63	4.45	15.6	0.06	<0.05	0.93	<0.05	<0.05	10.4
152.8	9A	10.5	4.62	3.63	16.3	0.05	0.17	1.09	<0.05	<0.01	9.80
153.4	10C	13.4	7.14	5.70	20.0	0.07	<0.05	0.84	<0.05	<0.05	10.1
153.9	10B	13.7	4.22	6.36	17.6	0.06	0.18	1.42	(0.07)	<0.01	16.4
154.5	10A	13.0	5.64	5.06	16.3	0.06	0.19	1.20	<0.05	<0.05	14.7
155.4	11C	12.5	(4.60)	3.60	12.1	0.04	<0.05	0.79	(0.04)	<0.01	15.1
155.9	11B	12.9	(3.60)	3.5	10.9	0.05	<0.05	0.94	<0.05	<0.05	14.9

Table B.4. Major Cation Composition of 1:1 Water Extracts from Borehole 41-09-39 Sidewall Cores and Extension Sleeves (3 Sheets)

Depth (ft bgs)	Sample ID	Calcium (ppm)	Potassium (ppm)	Magnesium (ppm)	Sodium (ppm)	Strontium (ppm)	Aluminum (ppm)	Boron (ppm)	Iron (ppm)	Manganese (ppm)	Silicon (ppm)
Extension (Cont'd)											
156.4	11A	11.3	(3.40)	2.51	6.63	0.04	0.01	0.96	<0.05	<0.05	10.9
156.8	12B	12.1	8.16	4.43	49.6	0.06	<0.05	0.92	<0.05	<0.05	14.0
157.1	12A	11.2	6.89	4.11	40.3	0.06	<0.05	1.12	<0.05	<0.05	13.1
157.2	13D	13.4	11.2	4.74	50.8	0.06	<0.05	0.62	<0.05	<0.05	12.5
157.7	13C	12.6	7.34	3.73	35.1	0.06	(0.08)	0.99	(0.06)	<0.05	13.8
158.2	13B	11.3	(4.30)	3.63	16.7	0.05	0.13	0.93	(0.09)	<0.05	15.9
162.3	16D	5.77	5.94	2.14	33.8	(0.03)	(0.08)	1.26	0.07	0.07	7.60
163.3	16B	5.40	3.14	1.60	7.58	(0.03)	0.08	0.81	0.08	(0.01)	11.1
163.8	16A	2.83	1.97	0.97	7.53	(0.01)	0.35	1.37	0.33	(0.03)	15.2
164.3	17D	9.52	6.00	3.02	29.3	0.05	(0.12)	0.93	0.14	(0.04)	11.3
165.3	17B	2.53	(2.00)	0.92	9.35	(0.01)	0.35	1.39	0.45	(0.02)	16.6
165.8	17A	2.75	2.00	0.92	7.72	(0.01)	0.60	1.28	0.71	(0.03)	16.6

Note: Values in parenthesis are near the detection limit but are considered good values.

NM = not measured.

Figure B.8. Dilution-Corrected Cation Concentrations at Borehole 41-09-39 in 1:1 Sediment to Water Extracts

Table B.5. Cesium-137 Activity in Borehole 41-09-39 Sidewall Cores and Extension Sleeves (2 Sheets)

Depth (ft bgs)	Sample ID	Cesium-137 (pCi/g)		Cesium-137 (pCi/g)	Depth (ft bgs)	Sample ID	Cesium-137 (+/- pCi/g)		Cesium-137 (pCi/g)	Depth (ft bgs)	Sample ID	Cesium-137 (pCi/g)		Cesium-137 (+/- pCi/g)	Cesium-137 (pCi/g)
		Wet Wt.	Error				Wet Wt.	Error				Dry Wt.	Dry Wt.		
Sidewall															
25.5	15A/B/C	5.50E+02	9.70E+00	6.06E+02	151.8	9B	9.54E+01	1.83E+00	NM	183	35B	3.21E-01	5.49E-02	3.32E-01	Cesium-137 (pCi/g)
44.5	14A/B/C	1.01E+03	1.83E+01	1.11E+03	152.8	9A	1.67E-01	1.24E-01	1.82E-01	183.3	35A	<MDA		<MDA	
56.5	13A/B/C	2.36E+04	5.27E+02	2.60E+04	152.9	10D	1.12E+02	2.57E+00	NM	183.9	36C	1.75E-01	3.95E-02	1.81E-01	
61.5	12A/B/C	1.13E+05	2.19E+03	1.25E+05	153.4	10C	7.13E-02	2.33E-02	7.95E-02	184.6	36B	4.89E-01	4.97E-02	4.99E-01	
65.5	11A/B	5.68E+05	1.06E+04	6.26E+05	153.9	10B	<MDA		<MDA	185	36A	<MDA		NM	
66	11C	3.71E+06	6.89E+04	4.09E+06	154.5	10A	1.98E-02	3.67E-02	2.39E-02	185.8	37D	1.57E-01	3.51E-02	1.59E-01	
69.5	10A/B/C	8.61E+03	1.10E+02	9.49E+03	155.1	11D	1.75E+00	1.70E-01	1.84E+00	186.2	37C	<MDA		<MDA	
74.5	9A/B/C	2.13E+06	3.94E+04	2.34E+06	155.4	11C	<MDA		<MDA	186.8	37B	<MDA		<MDA	
79.5	8A/B/C	2.32E+06	4.54E+04	2.56E+06	155.9	11B	<MDA		<MDA	187.2	37A	<MDA		<MDA	
82.5	7A/B/C	1.60E+07	4.31E+05	1.76E+07	156.4	11A	9.82E+00	2.94E-01	1.03E+01	187.8	38C	2.91E-01	3.23E-02	2.99E-01	
90	6A/B	3.97E+04	5.32E+02	4.38E+04	156.8	12B	7.38E+01	1.16E-01	7.89E+01	188.3	38B	<MDA		<MDA	
95.5	3A/B/C	3.40E+04	4.66E+02	3.82E+04	157.1	12A	7.31E+01	9.69E-01	7.79E+01	188.7	38A	<MDA		<MDA	
102.5	5A/B/C	1.44E+06	2.83E+04	1.62E+06	157.2	13D	5.56E+01	7.80E-01	5.92E+01	189.2	39B	3.72E-01	4.12E-02	3.78E-01	
108.5	4A/B/C	3.00E+05	7.54E+03	3.37E+05	157.7	13C	1.02E+01	2.45E-01	1.06E+01	189.5	39A	2.84E-01	3.72E-02	2.89E-01	
112	2B/C	1.32E+03	2.35E+01	1.49E+03	158.2	13B	1.15E+00	7.46E-02	1.21E+00	190.7	40A	<MDA		<MDA	
127.4	1A/B/C	3.73E+03	6.40E+01	4.20E+03	158.7	13A	3.13E-01	3.83E-02	NM	193.3	45A	4.40E-01	4.72E-02	4.63E-01	
Extension															
131.1	1C-L	3.24E+05	4.79E+03	NM	159	14D	NM		NM	195.9	47D	6.34E-02	1.87E-02	6.90E-02	
131.1	1C-D	7.96E+04	1.21E+03	NM	159.4	14C	2.68E+00	1.08E-01	2.84E+00	196.4	47C	<MDA		<MDA	
131.7	1B-1	2.08E+06	3.58E+04	2.35E+06	160	14B	<MDA		<MDA	196.9	47B	<MDA		<MDA	
131.7	1B-2	9.29E+02	1.41E+01	NM	160.6	14A	<MDA		<MDA	197.4	47A	1.92E-02	6.11E-03	2.01E-02	
133.2	2D	4.80E+04	6.44E+02	6.50E+04	162.3	16D	2.24E+00	8.25E-02	2.49E+00	198.8	49C	<MDA		NM	
133.7	2C	2.66E+04	4.09E+02	3.15E+04	162.8	16C	2.28E+00	1.04E-01	2.61E+00	199.1	49B	1.65E-01	3.23E-02	1.79E-01	
133.7	2C-2	1.16E+06	1.70E+04	1.47E+06	163.3	16B	4.56E+00	3.03E-02	4.75E+00	199.1	49A	9.66E-02	2.60E-02	1.06E-01	
134.2	2B	2.27E+03	3.25E+01	2.60E+03	163.8	16A	<MDA		<MDA	199.4	50B	2.49E-01	6.19E-02	2.66E-01	
134.7	2A	5.73E+01	1.14E+00	6.65E+01	164.3	17D	1.86E+00	8.63E-02	1.95E+00	199.4	50A	<MDA		<MDA	
					164.8	17C	9.31E-01	6.17E-02	9.63E-01	200.2	52B	<MDA		<MDA	
					165.3	17B	6.46E-02	2.98E-02	6.32E-02	200.7	52A	2.06E-01	3.55E-02	2.23E-01	

Table B.5. Cesium-137 Activity in Borehole 41-09-39 Sidewall Cores and Extension Sleeves (2 Sheets)

Depth (ft bgs)	Sample ID	Cesium-137 (pCi/g)			Depth (ft bgs)	Sample ID	Cesium-137 (pCi/g)			Depth (ft bgs)	Sample ID	Cesium-137 (pCi/g)		
		Wet Wt.	Error	Cesium-137 (+/- pCi/g)			Wet Wt.	Error	Cesium-137 (+/- pCi/g)			Wet Wt.	Error	Cesium-137 (+/- pCi/g)
135.2	3B	2.29E+03	4.04E+01	NM	165.8	17A	<MDA		<MDA	202.5	54B	4.85E-02	3.93E-02	5.17E-02
135.9	3A	2.93E+03	3.79E+01	3.31E+03	166.1	18D	3.42E-01	8.96E-02	NM	202.5	54A	2.18E-02	1.27E-02	2.30E-02
137.0	4D	NM		NM	166.6	18C	<MDA		<MDA	204.3	56C	<MDA		<MDA
137.4	4C	<MDA		<MDA	167.1	18B	<MDA		<MDA	205	56B	1.04E-01	5.05E-02	1.11E-01
138.0	4B	4.31E+01	6.62E-01	4.81E+01	167.7	18A	5.12E-02	6.11E-02	5.24E-01	205.6	56A	3.45E-02	1.31E-02	3.64E-02
138.7	4A	4.76E-01	6.19E-02	5.86E-01	169.2	20D	1.60E+00	7.94E-02	NM	207.6	58D	5.27E-02	2.07E-02	5.77E-02
139.9	5D	3.63E+01	5.34E-01	4.14E+01	169.4	20C	1.42E+00	1.14E-01	NM	208.1	58C	1.03E-01	3.93E-02	1.13E-01
140.3	5C	1.54E+01	3.11E-01	1.76E+01	169.7	20B	1.75E+00	8.73E-02	NM	208.6	58B	<MDA		<MDA
140.9	5B	6.93E+01	1.06E+00	7.81E+01	169.9	20A	2.94E-01	3.37E-02	3.02E-01	209	58A	<MDA		<MDA
141.5	5A	3.61E+00	1.50E-01	3.97E+00	171.3	22C	4.81E-01	7.19E-02	5.08E-01	209.4	59D	<MDA		<MDA
141.9	6F	1.39E+02	2.92E+00	1.54E+02	172	22B	4.19E-01	3.98E-02	4.42E-01	209.8	59C	<MDA		<MDA
142.4	6E	2.69E+00	1.57E-01	2.96E+00	172.7	22A	<MDA		NM	210.4	59B	<MDA		<MDA
143.3	6D	1.10E-01	3.69E-02	1.34E-01	178.2	28A	5.78E-01	6.25E-02	6.24E-01	210.9	59A	<MDA		<MDA
144.1	6C	1.38E+02	2.99E+00	1.74E+02	178.8	30C	5.39E-01	8.53E-02	5.76E-01	211.7	62B	2.87E-02		3.10E-02
144.7	6B	<MDA		<MDA	179.2	30B	<MDA		<MDA	212.1	62A	<MDA		<MDA
145.2	7E	4.21E+00	1.48E-01	4.57E+00	179.7	30A	<MDA		<MDA	212.9	64B	4.01E-02	3.37E-02	4.51E-02
145.8	7D	2.06E-01	2.05E-01	2.19E-01	180.2	31B	6.53E-01	8.02E+00	6.81E-01	213.3	64A	2.39E-02	1.18E-02	2.71E-02
146.4	7C	<MDA		<MDA	180.5	31A	5.18E-01	7.34E-02	5.37E-01	214.1	63B	2.31E-01	3.52E-02	2.49E-01
148.3	8C	2.04E+01	3.96E+00	2.19E+01	181.1	32B	6.25E-01	1.07E-01	6.58E-01	214.3	65A	9.05E-02	2.62E-02	9.83E-02
149.9	8B	1.27E+01	2.99E-01	1.39E+01	181.5	32A	1.53E-01	2.87E-02	1.58E-01	215	67*	1.13E-01	9.25E-02	NM
151.1	9C	1.09E+03	2.17E+01	1.23E+03										

Note: Sleeves 1C and 1B were partially filled and were compressed materials from the pile driving of the original casing. 1C-L and 1C-D represent light and dark compressed sediments. 1B-1 and 1B-2 were two distinctly different grain-sized compressed materials. 2C-2 was a fine-grained lens of silt within a fine sand matrix.

67* = clean out material in saturated sediments.

MDA = Minimum detectable cesium-137 activity; less than 2.00E-02 pCi/g.

NM = not measured.

Figure B.9. Cesium-137 Activity in Sediment versus Lithology and Depth

ote: A shows linear scale and B shows log scale.

Table B.6. Trace Metal Composition of 1:1 Water Extracts and Porewaters from Borehole 41-09-39 Sidewall Cores and Extension Composites (2 Sheets)

Composite Depth (ft bgs)	1:1 Extract ID	ICP-MS							Molybdenum (ppb)
		Technetium-99 (pCi/L)	Chromium (ppb)	Cobalt (ppb)	Nickel (ppb)	Zinc (ppb)	Arsenic (ppb)	Selenium (ppb)	
Sidewall									
25.5	15A/R/C	<1.0E+03	<0.5	(3.00)	<100	(68.0)	26.0	<5	14.0
44.5	14A/B/C	<1.0E+03	(2.89)	(1.00)	<100	(65.0)	14.9	<5	74.6
56.5	13A/B/C	<1.0E+03	(3.47)	<50	<100	(53.0)	0.77	<5	62.6
	13 UFA	2.88E+05	6463	<85	(9.00)	109	(4.33)	4457	104
61.5	12A/B/C	7.0E+02	(8.15)	(3.00)	<100	(56.0)	4.00	<5	24.9
65.5	11A/B	4.1E+03	344	(2.00)	(4.00)	(104)	24.3	<5	304
66	11C	7.8E+03	342	(1.00)	(2.00)	(102)	15.8	<5	93.4
69.5	10A/B/C	5.5E+03	5070	(7.00)	<100	(86.0)	30.0	<5	516
74.5	09A/B/C	7.7E+03	4091	(5.00)	(4.00)	(51.0)	24.3	<5	552
79.5	08A/B/C	1.8E+04	718	(1.00)	(2.00)	(49.0)	7.84	(4.86)	1003
	8 UFA	5.17E+05	20850	<156	(0.10)	1848	(8.13)	(74.2)	2596
82.5	07A/B/C	3.9E+05	745753	96.0	(6.0)	(66.0)	7.63	85.7	6378
90	06A/B	2.7E+06	711595	86.0	(6.0)	(88.0)	<5	135	2911
	6 UFA	2.48E+07	5627500	<453	(4.10)	944	264	1218	5032
95.5	03A/B/C	7.1E+06	260333	(30.0)	<100	(83)	<5	219	427
102.5	05A/B/C	6.1E+06	527799	60.0	<100	(112)	<5	228	1575
108.5	04A/B/C	1.2E+07	481344	63.0	(5.00)	(60)	<5	388	604
	4 UFA	9.40E+07	3183229	25917	29113	23519	62819	283662	943427
112	02B/C	8.6E+06	175630	25.0	<100	(50)	<5	288	1770
	2 UFA	1.23E+08	1795521	(657)	(4.10)	(332)	685	5074	(102)

Table B.6. Trace Metal Composition of 1:1 Water Extracts and Porewaters from Borehole 41-09-39 Sidewall Cores and Extension Composites (2 Sheets)

Composite Depth (ft bgs)	1:1 Extract ID	ICP-MS							
		Technetium-99 (pCi/L)	Chromium (ppb)	Cobalt (ppb)	Nickel (ppb)	Zinc (ppb)	Arsenic (ppb)	Selenium (ppb)	Molybdenum (ppb)
127.4	01A/B/C	3.3E+05	11.47	(0)	<100	(89)	1.05	31.5	167
Extension *									
133.2	2C/D	1000± 2500	3.00	6.86	<5	32.0	NA	<10	121
134.2	2A/B	5650±2200	<0.5	<0.5	<5	7.00	NA	<10	15.2
135.2	3A/B	2720±2500	<0.5	<0.5	<5	22.0	NA	<10	58.0
153.9	10A/B	3900±5200	<0.5	<0.5	<5	11.0	NA	<10	31.1
156.8	12A/B	380±2900	<0.5	<0.5	<5	7.00	NA	<10	87.1
165.3	17A/B	9320±12800	<0.5	<0.5	<5	14.0	NA	<10	13.0
188.3	38A/B	50±2800	<0.5	<0.5	<5	6.00	NA	<10	22.0
196.9	47A/B	(-190)±4700	<0.5	<0.5	<5	13.5	NA	<10	11.7
208.6	58A/B	(-470)±3800	<0.5	<0.5	<5	10.2	NA	<10	9.80

*For technetium-99 the borehole extension samples were analyzed by wet chemical separations and liquid scintillation counting. Samples were analyzed in duplicate and mean and uncertainty are presented. The deepest two composites yielded negative values. The technique is not as sensitive as the ICP-MS data. Units for technetium-99 are pCi/L and not mass units.

Highlighted pairs are chemical analyses of soil water derived from a common soil in two ways, by 1:1 water extraction and by direct removal of porewater by centrifugation using the unsaturated flow apparatus (UFA).

ICP = inductively coupled plasma.

MS = mass spectrometer.

NA = not analyzed.

The primary zone of true contamination is considered to be in subunit H1 and the upper half of subunit H2 between 18 and 39 m (60 and 127 ft) bgs. In this zone three peaks occur at 20, 25, and 31 m (66, 82.5, and 102 ft) bgs at concentration levels of 4×10^6 , 2×10^7 , and 2×10^6 pCi/g. Overall, the vast majority of cesium-137 mass resides in subunit H1 between 20 and 26 m (66 and 84 ft) bgs. Just below these peaks, cesium-137 concentrations drop by orders of magnitude.

The primary zone of elevated technetium-99 concentration (listed as pCi/L in Table B.6) lies between 24 and 39 m (79 and 127 ft) bgs, where maximum concentrations of greater than 1×10^7 pCi/L are measured at 33 m (108 ft) bgs. Water extract concentrations of technetium-99 with depth are shown in Figure B.10. This pattern closely mimics the nitrate concentration distribution. Chromium concentration values increase above background beginning at 20 m (66 ft) bgs and reach maximum concentrations of greater than 100,000 $\mu\text{g/L}$ between 22 and 38 m (82 and 112 ft) bgs. The occurrence of the maximum chromium range slightly higher in the soil column relative to technetium-99 indicates some retarding chemical mechanism has slowed chromium migration relative to technetium-99. Work completed by the Hanford Science and Technology (S&T) Program (Appendix D, Section D.4.1) indicates that iron(II)-rich minerals in the vadose zone soil reduce the oxidation state of a fraction of the chromium in solution from +6 to +3. In the +3 state, chromium is removed from solution by sorption or co-precipitation in iron(II)-rich minerals.

B.2.4 CHEMICAL INTERACTIONS

No specific experiments were completed on soils from borehole 41-09-39 to quantify geochemical reactions influencing contaminant migration. Dominant chemical reactions affecting radionuclides and tank fluid chemicals are inferred from the relative location of these constituents in the soil column, comparison of acid-leachable versus water-leachable concentrations for specific contaminants, and general knowledge of the tank fluid chemistry. Greater contaminant mobility is inferred from the occurrence of high concentration zones deeper in the vadose zone and smaller differences in dissolved concentrations leached by water versus acid.

Generally speaking, the data suggest that tank SX-108 fluid chemistry had a substantial but limited effect on contamination behavior at borehole 41-09-39. Given the distance between borehole 41-09-39 and the tank SX-108 bottom, the presence of very high concentrations of cesium-137 in subunit H1 in this borehole shows that cesium-137 was initially highly mobile in the leaked tank fluid. Various types of sorption experiments completed by the S&T activity (Appendix D, Section D.3.0) shows that the very high concentrations of cesium-137, sodium and to a lesser extent potassium in the tank SX-108 fluid created local conditions where sodium preferentially occupied soil sorption sites in soils and preventing cesium-137 sorption. These conditions were short-lived and confined to subunit H1 and the top part of subunit H2 as shown by the current limited distribution of cesium-137. Over time natural infiltration and recharge subsequently separated sodium from cesium-137, permitting cesium-137 to sorb in situ. The current degree of cesium-137 mobility was determined by comparing the amount of cesium-137 removed by water versus total activity measured by gamma. The in situ distribution coefficient for cesium-137 varies from 4 to 25 mL/g in the sediments between 27 and 34 m (90 and 112 ft) bgs where the bulk of the tank fluid with high salinity resides. Above and below this depth range cesium-137 in situ distribution coefficient values are usually much larger (greater than 1000 mL/g) because the pore fluids do not contain high sodium concentrations that compete for adsorption sites.

Figure B.10. Technetium-99 Activity in Porewater in Borehole 41-09-39

Tank fluids also increased amounts of other constituents to the soil column but had little effect on the chemical behavior of contaminants other than cesium-137 in the sense that chemical reactions between tank fluid constituents and the soil column environment were largely controlled by soil-soil water reactions. Constituent anions (e.g., nitrate and technetium-99) have migrated the most rapidly and mark the leading edge of vertical tank fluid migration. The technetium-99 in situ distribution coefficient was determined by comparing acid versus water leached concentrations and varies from 0.01 to about 5 mL/g over the whole zone of contamination. Chromium was slightly retarded relative to technetium-99 and nitrate, presumably because of oxidation reduction, allowing fixation on soil. Generally, the in situ distribution coefficient values were negative except for the soil sample at 24 m (80 ft) bgs where the distribution coefficient value greater than 20 mL/g was estimated.

Other constituent cations have migrated varying distances depending on the strength of retardation mechanisms. Sodium concentrations, being relatively high, successfully competed for sorption sites in vadose zone soils, were somewhat retarded. Calcium, magnesium, and indigenous strontium were displaced by sodium and pushed ahead of sodium during migration.

B.2.5 GROUNDWATER MEASUREMENTS

One sample of groundwater was taken from borehole 41-09-39 prior to decommissioning. Small concentrations of technetium-99, tritium, and nitrate are present in the water. There is no indication of a tank waste source. A more likely source is the upgradient crib 216-S-25.

B.3.0 BOREHOLE 299-W23-19

This section summarizes data reported in *Geologic and Geochemical Data Collected from Vadose Zone Sediments from Borehole 299-W23-19 [SX-115] in the S/SX Waste Management Area and Preliminary Interpretations* (Seme et al. 2001c) except for the groundwater sample data, which are reported in the RCRA groundwater quality assessment report (Johnson and Chou 2001). Borehole 299-W23-19 was completed to further characterize the nature and extent of vadose zone contaminants supplied by a tank SX-115 leak. The most significant data provided by this characterization effort were soil measurement of radionuclides and chemicals attributed to the tank SX-115 leak. Elevated concentrations of several constituents were primarily measured in soils between 22 and 48 m (73 and 156 ft) bgs. This depth interval includes subunits H1 and H2 and subunit PPlz. The primary radionuclide present in this zone is technetium-99. Cesium-137 is present in very small concentrations at the top of this contaminated soil zone. The primary chemical characteristics attributed to tank fluid-soil interaction at different locations within this zone are elevated pH, sodium, chromium, nitrate, and chloride.

The absence of tank fluid constituents in the PPlc subunit of the Plio-Pleistocene unit and the Ringold Formation down to the water table is significant because of the very **high** technetium-99 content in the first water samples taken from borehole 299-W23-19. Subsequent conversion of this borehole into a monitoring well and continued groundwater sampling has revealed sustained high technetium-99 content. Also, the **technetium-99/nitrate** ratios at this well are indicative of a tank waste source because they are significantly greater than ratios in surrounding wells (Figure C.25) indicating a different source that is enriched in technetium-99. Also, the well ratio values (0.11 pCi/μg or 110 pCi/mg) are essentially the same as the ratio values in water extract data from soil samples in the high technetium-99/nitrate zone of borehole 299-W23-19 (Table 3.5). Assuming that both vadose zone and groundwater contamination from this borehole come from the tank SX-115 leak, a complicated migration path is indicated which must include both lateral and vertical movement.

Moisture content and matric potential measurements are consistent with recent high recharge through the soil column at this location imposed by one or more leaking water lines. Moisture contents are generally above average in the soil column and matric suction measurements indicate drainage is occurring throughout the soil column. These data and the presence of contaminants in other wells downgradient of tank SX-115 (Appendix C, Section C.7.0) present a logical pattern of accelerated migration of tank SX-115 fluid contaminants to and subsequent limited distribution within the unconfined aquifer.

B.3.1 GEOLOGY

Borehole 299-W23-19 was drilled using air-rotary techniques. Samples were collected via the split spoon technique in as near-continuous manner as possible. The split-spoon samplers were driven into the formation ahead of the casing. After the samples were extracted from the hole, a standard bit was lowered in the hole and materials removed to the depth at which the sampling stopped. The casing was driven to that same depth and the process repeated. Samples were attempted in the Ringold Formation but the cemented gravels proved too much for the technique. Samples were collected from near the historic high groundwater elevation and again at the water table.

B.3.1.1 Backfill

Backfill material extends from the surface to 18.7 m (61.5 ft) bgs. The material consists of non-cohesive sand with variable silt and minor pebbles. There was little variation in the geophysical logs of borehole 299-W23-19 confirming its relatively uniform nature.

B.3.1.2 Hanford formation

All three Hanford formation subunits (H1a, H1, and H2) were present and sampled.

- Subunit H1a – Subunit H1a occurs from 18.7 to 23.8 m (61.5 to 78 ft) bgs in borehole 299-W23-19. The subunit consists of several upward fining, coarse sand to silty fine sand rhythmites. Sedimentary structures within these beds range from planar-laminated sand at the base to wavy ripple cross-laminated sand and silt at the top. Grain sizes within individual beds are gradational but the upper and lower boundaries of individual beds are sharp, where coarse sand associated with the overlying bed lies in direct contact with fine material from the underlying bed. Higher moisture is usually associated with the finer grained upper portions of these graded beds.
- Subunit H1 – Subunit H1 occurs from 23.8 to 28.7 m (78 to 94 ft) bgs in borehole 299-W23-19. The subunit is predominantly a pebbly, medium- to coarse-grained sand. At least two layers of fine sand to muddy sand are present in the sequence.
- Subunit H2 – Subunit H2 occurs from 28.7 to approximately 37.2 m (94 to 122 ft) bgs in borehole 299-W23-19. The subunit is predominantly fine grained, consisting of stratified fine sand to silty fine sand. Several coarser sand interbeds are present toward the top of the sequence. Graded rhythmites development is not as obvious in subunit H2 as in subunit H1a. Instead, there appear to be many irregular subtle gradations, mostly between platy (laminated), silty-fine to very-fine sand and occasionally medium to coarse sand. The calcium carbonate content of this unit is relatively low. Based on an increase in total gamma activity on geophysical logs the base of subunit H2 has been identified at 37.2 m (94 ft) bgs in an interval where there was no core recovery.

B.3.1.3 Plio-Pleistocene Unit

The two Plio-Pleistocene unit subunits are the upper subunit PPlz, characterized by a relatively high silt content and the lower subunit PPlc, characterized by secondary, pedogenic, calcium-carbonate cement.

- Subunit PPlz – Subunit PPlz is interpreted to extend from 37.2 to 47.5 m (122 to 156 ft) bgs at borehole 299-W23-19. The subunit consists of mostly fine to very fine sand that is intercalated with silty fine sand to silt/clay. Most beds display well-preserved stratification, except within paleosols where the bedding has been disturbed by blocky soil-ped development, mottling, and/or bioturbation associated with pedogenesis. Dark carbonaceous aggregates (i.e., decomposed organic matter) and secondary iron-oxide and manganese-oxide staining are also common.

- **Subunit PPlc** – Subunit PPlc is interpreted to extend from 47.5 to **48.8** m (156 to 160 ft) bgs at borehole 299-W23-19. At this site subunit PPlc consists of weathered, dark-olive gray, loose, basaltic, pebbly sand interspersed with more indurated layers of mud and calcium carbonate. The geologic interpretation of this unit at this location differs from elsewhere in the vicinity of the SX tank farm. In this borehole the unit is highly basaltic and coarse in nature; elsewhere the unit is typically a massive carbonate facies. Additionally, the calcium carbonate does not occur as a single, well-developed caliche layer but appears to occur as stringers within the coarse-grained basaltic alluvium.

B.3.1.4 Ringold Formation

The remainder of the vadose zone at borehole 299-W23-19 below 48.8 m (160 ft) bgs is composed of Ringold Formation, member of Wooded Island, unit E as described in *Vadose Zone Geology of Boreholes 299-W22-50 and 299-W23-19-S-SX Waste Management Area Hanford Site, South-Central Washington* (Lindsey et al. 2000). The recovered materials consist predominately of fluvial, weakly cemented sandy gravel to strongly cemented, matrix-supported conglomerate. The gravel/conglomeratic facies is both clast supported and matrix supported. The matrix ranges from sandy mud, to muddy fine sand, to well-sorted quartz-rich fine or medium sand, to very coarse sand. The gravel clasts are subrounded to rounded and range up to 70 mm (3 in.) in diameter. The clasts are composed predominately of quartzite, basalt, and granite. In places, the basalt and granitic clasts are highly weathered, and iron oxide staining is common.

B.3.2 GEOPHYSICAL AND PHYSICAL PROPERTY MEASUREMENTS

Downhole geophysical measurements included a high-purity germanium spectral gamma log, a neutron-neutron log, a neutron-gamma log, and a temperature log. The total gamma log (derived from the spectral gamma logs) and the neutron-neutron log are shown in Figure B.11. In borehole 299-W23-19 where negligible manmade gamma contamination is present, the gamma data track relative potassium-40 concentrations and higher potassium-40 concentrations indicate silt-rich layers. In this case the PPlz subunit contains maximum potassium-40 concentrations. The spike at 30 m (100 ft) bgs is considered to be an artifact of the measuring event, not a real indicator of high potassium-40 concentration. The neutron-neutron log shows qualitative relative moisture content and is consistent with laboratory-measured moisture contents shown in the adjacent column (moisture) and provided in Table B.7. The neutron-gamma log (not shown; see Lindsey et al. 2000) provides an indication of relative amounts of silica, calcium and hydrogen in the formation. A maximum temperature of 82 °F (28 °C) was measured at 20 m (65 ft) bgs, about the same depth as the tank bottom indicating that residual heat loading from the tank waste continues to have a local effect.

Soil suction measurements were completed for several soil samples. Soil suction values are plotted as a function of depth in Figure B.12. All values plot to the left of the drainage curve indicating that drainage is occurring in the soil column at borehole 299-W23-19. Conversely, in two RCRA groundwater monitoring wells east of WMA S-SX, where no indication of manmade discharge to the soil column is known to occur, drainage is not indicated for soil samples below the Plio-Pleistocene unit.

Figure B.11. Borehole 299-W23-19 Lithology, Stratigraphy, and Moisture Content (wt%) Distribution as a Function of Depth

Table B.7. Moisture Content of Sediments from Borehole 299-W23-19 (2 Sheets)

Sample ID	Depth (ft bgs)	Moisture (%)	Sample ID	Depth (ft bgs)	Moisture (%)	Sample ID	Depth (ft bgs)	Moisture (%)	Sample ID	Depth (ft bgs)	Moisture (%)	Sample ID	Depth (ft bgs)	Moisture (%)	Sample ID	Depth (ft bgs)	Moisture (%)
01F	6.55	6.80	10C	36.35	9.42	18E	69.45	9.81	26E	102.95	7.04	31C	131.15	8.98	38F	152.60	13.47
01E	7.05	4.96	10B	36.85	9.15	18D	69.95	12.32	26D	103.45	3.79	31B	131.65	5.43	38E	153.10	14.07
01D	7.55	5.79	10A	37.35	8.38	18C	70.45	15.66	26C	103.95	6.99	31A	132.15	16.92	38D	153.60	15.96
01C	7.86	6.89	11F	40.85	6.20	18B	70.95	14.86	26B	104.45	8.99	32G	132.75	4.97	38C	154.10	17.95
01B	8.34	4.41	11E	41.35	6.51	18A	71.45	19.61	26A	104.95	6.81	32F	133.25	5.47	38B	154.60	19.15
01A	9.54	4.56	11D	41.85	8.18	19J	72.25	5.59	27J	105.55	21.03	32E	133.75	13.28	38A	155.10	26.11
03K	11.35	6.96	11C	42.35	11.00	19I	72.75	4.82	27I	106.05	12.76	32D	134.25	7.82	38	155.55	21.95
03J	11.85	7.49	11B	42.85	7.28	19H	73.25	3.61	27H	106.55	4.45	32C	134.75	8.60	39D	155.35	6.97
03I	12.35	7.59	11A	43.35	5.53	19G	73.75	12.15	27G	107.05	6.66	32B	135.25	13.33	39C	155.85	7.80
03H	12.85	6.81	13G	43.85	7.02	19F	74.25	14.11	27F	107.55	5.43	32A	135.80	17.27	39B	156.35	3.49
03G	13.35	7.18	13F	44.35	6.23	19E	74.75	14.20	27E	108.05	4.18	33I	136.65	9.81	39A	156.85	19.81
03F	13.85	7.45	13E	44.85	5.44	19D	75.25	12.92	27D	108.55	9.55	33H	137.15	13.86	40B	157.75	4.88
03E	14.35	5.73	13D	45.35	9.72	19C	75.75	6.05	27C	109.00	8.69	33G	137.65	15.57	40A	158.25	4.65
03D	14.85	7.25	13C	45.85	9.95	19B	76.25	3.84	27B	109.55	7.29	33F	138.15	9.90	40	158.65	10.12
03C	15.35	7.53	13B	46.35	8.80	19A	76.75	4.18	28G	110.25	8.42	33E	138.65	7.60	17SK	159.75	8.39
03B	15.85	5.13	13A	46.85	12.89	20H	78.25	3.32	28F	110.75	8.71	33D	139.15	4.95	18SKA	161	6.89
03A	16.35	5.99	14J	50.15	8.48	20G	78.75	5.26	28E	111.25	14.04	33C	139.65	7.99	18SKB	161.00	5.24
04H	17.15	5.07	14I	50.65	8.00	20F	79.25	7.32	28D	111.75	10.03	33B	140.15	15.49	18SKC	166.50	2.95
04G	17.65	5.63	14H	51.15	7.41	20E	79.75	12.58	28C	112.25	7.10	33A	140.65	11.49	19SKA	166.50	1.35
04F	18.15	7.24	14G	51.65	9.89	20D	80.25	16.67	28B	112.75	8.30	35K	141.05	11.47	19SKB	176.00	1.24
04E	18.65	6.86	14F	52.15	11.01	21E	82.00	2.58	28A	113.20	12.75	35J	141.35	13.24	41A	184.45	3.95
04D	19.15	7.26	14E	52.65	6.80	21D	83.00	3.55	29I	113.85	8.91	35I	141.85	24.48	19SKC	185	0.88
04C	19.65	8.72	14D	53.15	5.28	21C	84.00	4.31	29H	114.35	5.78	35H	142.35	27.23	20SKA	185	1.28
04B	20.15	7.94	15B	54.12	6.23	21B	85.00	2.94	29G	114.85	4.22	35G	142.85	27.15	20SKB	189.5	1.14

Table B.7. Moisture Content of Sediments from Borehole 299-W23-19 (2 Sheets)

Sample ID	Depth (ft bgs)	Moisture (%)	Sample ID	Depth (ft bgs)	Moisture (%)	Sample ID	Depth (ft bgs)	Moisture (%)	Sample ID	Depth (ft bgs)	Moisture (%)	Sample ID	Depth (ft bgs)	Moisture (%)
04A	20.65	7.25	15A	54.50	5.84	21A	86.00	2.89	29F	115.35	4.97	35F	143.35	26.80
05E	22.85	8.48	16B	56.95	6.59	22E	87.10	7.72	29E	115.85	5.51	35E	143.85	25.08
05D	23.55	8.87	16A	57.45	6.32	22D	88.10	16.49	29D	116.35	5.60	35D	144.35	16.57
05C	24.65	7.77	17J	61.75	5.33	22C	10	5.65	29C	116.85	9.08	35C	144.85	16.25
05B	25.75	7.42	17I	62.25	5.70	22B	91.10	8.12	29A+B	117.85	9.87	35B	145.35	11.50
05A	26.85	8.87	17H	62.75	5.18	22A	91.10	5.27	30G	123.85	7.86	35A	145.85	25.75
08C	27.55	8.15	17G	63.25	8.99	24C	93.00	8.01	30F	124.35	10.12	36F	146.45	15.67
08B	28.65	9.51	17F	63.75	11.77	24B	94.00	6.42	30E	124.85	10.07	36E	146.95	16.91
08A	29.75	9.13	17E	64.25	21.84	24A	95.00	9.25	30D	125.35	9.78	36D	147.45	9.36
09I	30.95	8.46	17D	64.75	20.18	25E	96.06	4.46	30C	125.85	13.18	36C	147.95	8.52
09H	31.45	9.69	17C	65.25	11.13	25D	97.06	4.47	30B	126.35	16.57	36B	148.45	22.95
09G	31.95	8.23	17B	65.75	10.30	25C	98.06	5.21	30A	126.85	13.86	36A	148.95	16.89
09F	32.45	8.00	17A	66.25	9.34	25B	99.06	5.12	31J	127.80	12.27	37E	149.15	13.30
09E	32.95	10.16	18K	66.45	13.04	25A	100.06	11.54	31I	128.15	7.26	37D	149.65	12.95
09D	33.45	9.18	18J	66.95	14.17	20D	100.45	12.18	31H	128.65	11.59	37C	150.15	15.33
09C	33.95	8.11	18I	67.45	17.48	26I	100.95	17.79	31G	129.15	15.12	37B	150.65	17.24
09B	34.45	8.73	18H	67.95	16.46	26H	101.45	7.98	31F	129.65	16.32	37A	151.15	13.73
09A	34.95	8.72	18G	68.45	5.16	26G	101.95	9.72	31E	130.15	15.09	38H	151.75	18.93
10D	35.85	8.96	18F	68.95	9.88	26F	102.45	11.96	31D	130.65	12.30	38G	152.10	21.31

Figure B.12. Soil Suction Profiles for Borehole 299-W23-19

Note: Dashed line is the equilibrium soil suction line. Drainage occurs only for values to left of the equilibrium line.

B.3.3 SOIL WATER CHEMISTRY MEASUREMENTS

In addition to soil physical property measurements (Section B.3.2), an extensive water chemistry analysis has been completed for borehole 299-W23-19 samples collected between 10 and 62 m (32 and 205 ft) bgs. The primary means of measuring porewater composition was to add deionized water to soil samples to generate enough water for performing analyses.

By back-calculating for the dilution introduced by the added water, 'true' concentrations were derived. For a few samples porewater was directly separated from the same soil sample or one nearby and analyzed directly. By comparing the dilution-corrected water extract data with the porewater data in these few samples, an indication of the closeness of the water extract chemistry to original water chemistry was determined. In general, comparisons were not exact but concentration values were generally within a factor of two or better, agreement improved with increasing constituent concentration, and both sets of data showed similar concentrations versus soil depth correlations. Thus, the water extract method is an effective tool for evaluating tank fluid interactions with vadose zone soil.

Water extract pH and electrical conductivity measurements with depth are listed in Table B.8 and graphed in Figure B.13. Elevated pH values (greater than 8) are measured between 23 and approximately 32 m (75 and 105 ft) bgs with maximum values (8.5 to 9.7) occurring primarily in subunit H1 between 23 and 26 m (75 and 86 ft) bgs. Because pH values are expected to decrease as increasing interaction with soil and soil water occurs, the location of maximum pH values suggests the approximate initial depth of tank fluid interaction with the vadose zone at this location. Increases in electrical conductivity values compared to undisturbed soil water values are also an indicator of tank fluid occurrence in soil. Substantive increases are measured between 22 and 48 m (73 and 156 ft) bgs with maximum values (approximately 20,000 to 40,000 $\mu\text{S}/\text{cm}$) between 37 and 46 m (123 and 150 ft) bgs in the silt-rich subunit PPlz. Maximum electrical conductivity values are an indicator of location for mobile tank fluid constituents and maximum vertical penetration of tank fluids.

Water extract anion concentrations as a function of depth are listed in Table B.9 and graphed in Figure B.14. The primary indicator of tank fluid occurrence is elevated nitrate concentrations which are measured in borehole 299-W23-19 between 22 and 48 m (73 and 156 ft) bgs with maximum values between 38 and 46 m (125 and 150 ft) bgs. Elevated levels of chloride (between 22 and 62 m [73 and 205 ft] bgs) and sulfate (between 22 and 62 m [73 and 190 ft] bgs) are also observed. Chloride maximum concentrations (between 38 and 46 m [125 and 150 ft] bgs) track closely with the nitrate at the Plio-Pleistocene unit and above. However, an additional peak occurs in the Ringold Formation between 51 and 58 m (166 and 190 ft) bgs. The sulfate peak occurs between 22 and 38 m (73 and 125 ft) bgs, a maximum concentration depth interval that does not coincide with chloride and nitrate. A secondary sulfate peak range occurs in the Ringold Formation between 51 and 58 m (166 and 190 ft) bgs, coincident with the secondary chloride peak.

Elevated concentrations of these anions do not provide a straightforward indication of tank fluid occurrence. Elevated concentrations of chloride and sulfate extend well into the Ringold Formation (to groundwater in the case of chloride), unlike nitrate. This observation suggests other sources of chloride and sulfate (e.g., U pond water) which as late as 1986 elevated the water table up to 55 m (182 ft) bgs. In the Hanford formation and the Plio-Pleistocene unit, chloride and sulfate concentrations may come from the tank fluid or may result from some interaction between tank fluid nitrate and indigenous chloride and sulfate that preferentially dissolves these anions.

Table B.8. Borehole 299-W23-19 Water Extract pH and Electrical Conductivity Values (2 Sheets)

Sample ID	Depth (ft bgs)	Dilution Factor	1:1 pH	1:1 EC ($\mu\text{S}/\text{cm}$)	Pore EC ($\mu\text{S}/\text{cm}$)	Sample ID	Depth (ft bgs)	Dilution Factor	1:1 pH	1:1 EC ($\mu\text{S}/\text{cm}$)	Pore EC ($\mu\text{S}/\text{cm}$)
09E	32.95	9.85	7.94	166	1635	31A	132.15	6.36	6.95	5198	33066
15A	54.50	17.13	7.25	233	3992	32D	134.25	11.80	6.96	1658	19561
16A	57.45	15.82	7.27	226	3576	32A	135.80	5.79	6.8	4973	28781
17J	61.75	18.84	7.57	153	2883	33G	137.65	6.43	6.82	4860	31270
17G	63.25	11.13	7.52	186	2071	33B	140.15	6.45	6.81	4840	31238
17F	63.75	8.53	7.41	217	1851	35K	141.05	8.72	6.9	4593	40058
17F-dup	63.75	8.56	7.1	211	1807	35IH-aft	141.85	6.30	6.88	4265	26852
17DE-aft	64.75	10.70	7.48	206	2204	35F-aft	143.35	7.18	6.93	3264	23439
17C	65.25	9.03	7.32	160	1445	35C	144.85	6.15	6.95	2830	17409
18I	67.45	5.74	7.44	243	1394	35A	145.85	3.89	6.86	4315	16781
18E	69.45	10.19	7.62	226	2302	36D	147.45	10.20	6.98	1593	16254
18CB	70.45	6.56	7.91	431	2826	36B	148.45	4.35	7.02	2655	11562
18CB-dup	70.95	6.56	7.46	413	2709	37D	149.65	7.72	6.96	3792	29278
19H	73.25	27.70	8.61	603	16701	38G	152.10	4.32	7.21	979	4232
19G	73.75	7.49	8.33	1207	9038	38E	153.10	7.11	7.37	624	4439
19F	74.25	7.09	7.71	1248	8847	38E-dup	153.10	7.11	7.43	604	4297
19D	75.25	9.61	9.35	1039	9980	38A-aft	155.10	10.92	7.04	280	3057
20F	79.25	9.47	9.12	1094	10364	39D	155.35	9.49	7.39	768	7288
20F-dup	79.25	9.38	9.15	1025	9617	39C	155.85	12.83	6.83	352	4516

Table B.8. Borehole 299-W23-19 Water Extract pH and Electrical Conductivity Values (2 Sheets)

Sample ID	D ₅₀ (%)	Dilution Factor	1:1 pH	1:1 EC (μS/cm)	Pore EC (μS/cm)	Sample ID	D ₅₀ (%)	Dilution Factor	1:1 pH	1:1 EC (μS/cm)	Pore EC (μS/cm)
20E	79.74	7.79	9.28	1014	7902	39C-dup	155.85	12.82	6.97	342	4385
20D	80.25	6.00	8.5	1198	7184	40B	157.75	20.49	7.68	201	4119
21A	86.00	13.58	9.72	762	10350	40	158.65	10.96	7.65	297	3256
22D	88.10	6.07	7.79	1328	8056	17SK	159.75	11.92	7.7	281	3350
24A	95.00	10.82	7.91	1023	11065	18SKA	161	14.68	7.64	251	3684
25B	99.06	14.17	9.08	693	9822	18SKB	161.00	19.78	7.05	252	4984
25B-dup	99.06	15.85	8.74	595	9430	18SKC	166.50	34.13	7.26	148	5051
25A	100.06	11.40	7.83	1071	12212	19SKA	166.50	74.25	7.24	124	9207
26E	102.95	13.75	8.93	639	8786	19SKB	176.00	80.64	7.26	116	9354
26A	104.95	12.21	9.31	592	7226	41A	184.45	25.37	7.9	85	2157
27G	107.05	15.02	7.84	944	14182	19SKC	185	114.65	8.38	85	9745
29DC	116.35	13.67	7.33	1124	15363	20SKA	185	78.06	7.62	93	7260
30GF	123.85	11.13	7.02	1922	21390	20SKB	189.5	82.45	7.43	101	8327
30D	125.35	6.78	6.96	3902	26448	42	194.55	17.10	7.7	142	2428
30B	126.35	6.03	6.61	5730	34580	43B	204.50	16.25	7.52	273	4435
31G	129.15	6.62	6.71	6907	45724	43A	205.15	41.39	7.86	112	4636

EC = electrical conductivity.

Figure B.13. Calculated and Actual Porewater pH and Electrical Conductivity Values for Borehole 299-W23-19 Sediments

Table B.9. Anion Content of Water Extracts of Borehole 299-W23-19 Sediments (3 Sheets)

Sample ID	Depth (ft bgs)	Dilution Factor	Water:Soil Ratio	1:1 Extracts (mg/L)								Dilution Corrected Porewater (mg/L)					
				Nitrate	Fluoride	Nitrite	Chloride	Sulfate	Phosphate	Alk*	Nitrate	Nitrite	Chloride	Sulfate	Phosphate	Fluoride	Alk*
09E	32.95	9.85	1.00	1.00	0.64	<0.04	0.16	2.34	0.14	124	10	<0.39	1.6	23	1.4	6.3	1219
15A	54.50	17.13	1.00	0.76	0.77	<0.04	0.71	11.66	<0.1	96	13	<0.69	12.2	200	1.7	13.2	1647
16A	57.45	15.82	1.00	3.10	0.78	<0.04	0.91	18.33	0.10	305	49	<0.63	14.4	290	1.6	12.3	4830
17J	61.75	18.84	1.00	1.35	0.45	<0.04	0.37	7.14	<0.1	58	25	<0.75	7.0	135	1.9	8.5	1101
17G	63.25	11.13	1.00	5.25	0.60	<0.04	0.39	11.86	0.12	83	58	<0.45	4.3	132	1.3	6.7	921
17F	63.75	8.53	1.00	8.83	0.72	<0.04	0.60	15.77	0.19	78	75	<0.34	5.1	135	1.6	6.1	664
17FDUP	63.75	8.56	1.01	8.3	0.73	<0.08	0.5	13.67	0.18		71	<0.69	4.3	117	1.5	6.3	
17C	65.25	9.03	1.00	12.43	0.55	<0.04	0.62	17.31	0.24	65	112	<0.36	5.6	156	2.2	5.0	586
18I	67.45	5.74	1.00	19.93	0.57	<0.04	0.91	25.14	0.44	78	114	<0.23	5.2	144	2.5	3.3	447
18E	69.45	10.19	1.00	10.26	0.54	<0.04	0.66	12.66	0.30	91	105	<0.41	6.7	129	3.1	5.5	928
18C	70.45	6.56	1.00	28.02	1.02	<0.04	1.20	22.91	1.24	160	184	<0.26	7.9	150	8.1	6.7	1047
18B	70.95	6.56	1.00	27.69	1.02	<0.08	1.28	23.02	1.76		182	<0.52	8.4	151	11.5	6.7	
19H	73.25	27.70	1.00	136.83	2.43	<0.1	2.05	15.71	0.62		3790	<2.8	56.8	435	17.2	67.3	
19G	73.75	7.49	0.86	400.86	2.54	<0.1	6.73	42.45	0.74		3002	<0.7	50.4	318	5.5	19.0	
19F	74.25	7.09	1.00	431.09	2.64	<0.04	6.69	44.49	<1	131	3056	<0.28	47.4	315	<7.1	18.7	931
19D	75.25	9.61	1.18	321.44	1.52	<0.1	4.6	28.31	0.89		3088	<1.0	44.2	272	8.5	14.6	
20F	79.25	9.47	0.76	292.01	3.35	<0.1	3.87	31.17	1.19		2766	<0.9	36.7	295	11.3	31.7	
20FDUP	79.25	9.38	1.04	250.53	4.36	<0.1	3.43	25.87	1.3		2351	<0.9	32.2	243	12.2	40.9	
20E	79.75	7.79	1.00	275.95	3.78	<0.1	3.43	27.1	1.37		2150	<0.8	26.7	211	10.7	29.5	
20D	80.25	6.00	1.00	358.65	2.01	<0.04	4.63	35.21	3.16	175	2151	<0.24	27.8	211	18.9	12.1	1051
21A	86.00	13.58	0.61	73.51	3.83	<0.1	1.21	12.68	0.67		998	<1.4	16.4	172	9.1	52.0	
22D	88.10	6.07	1.00	446	2.62	<0.04	6.46	44.80	1.61	182	2716	<0.24	39.5	274	10.7	15.9	1105
24A	95.00	10.82	1.00	340.37	0.72	<0.04	4.11	37.24	1.45	215	3682	<0.43	44.5	403	15.7	7.8	2320
25B	99.06	14.17	0.81	183.64	1.71	<0.1	3.42	33.28	0.83		2603	<1.4	48.5	472	11.8	24.2	

Table B.9. Anion Content of Water Extracts of Borehole 299-W23-19 Sediments (3 Sheets)

Sample ID	Depth (ft bgs)	Dilution Factor	Water:Soil Ratio	4.1.1 Extracts (mg/L)								Dilution Corrected Forewater (mg/L)							
				Nitrate	Fluoride	Nitrite	Chloride	Sulfate	Phosphate	Alk*	Nitrate	Nitrite	Chloride	Sulfate	Phosphate	Fluoride	Alk*		
25BDUP	99.06	15.85	0.97	141.66	1.83	<0.1	2.46	25.36	0.81		2245	<1.6	39.0	402	12.8	29.0			
25A	100.06	11.40	0.79	423.71	0.58	<0.1	6.94	61.74	<0.5		4831	<1.1	79.1	704	5.7	6.6			
26E	102.95	13.75	1.00	156.9	0.95	<0.1	3.16	34.49	1.28		2157	<1.4	43.4	474	17.6	13.1			
26A	104.95	12.21	1.00	75.31	1.06	<0.1	2.49	28.44	0.84		919	<1.2	30.4	347	10.3	12.9			
27G	107.05	15.02	1.00	342.38	<2	<0.04	4.71	39.20	1.07	611	5144	<0.60	70.8	589	16.1	<30	9174		
29D	116.35	13.67	1.00	467.69	0.35	<0.04	5.79	45.67	ND	49	6392	<0.55	79.1	624	ND	4.8	676		
30G	123.85	11.13	1.00	864.67	<0.4	0.72	9.55	83.98	1.72	84	9623	8.01	106.3	935	19.1	<4.5	936		
30D	125.35	6.78	0.79	2179.7	0.82	<0.1	17.81	89.94	<5		14774	<0.7	120.7	610	<33.9	5.6			
30B	126.35	6.03	1.00	3168.8	<0.2	42.80	25.28	39.80	0.91	83	19123	258.29	152.6	240	<5.5	<1.2	502		
30BDUP	126.35	6.03	1.00	3439.5	<0.2	31.17	26.88	43.8	3.49		20757	188.11	162.2	264	<21.1	<1.2			
31G	129.15	6.62	1.00	3932.5	<0.2	27.78	32.52	23.92	<1	66	26033	183.90	215.3	158	<6.6	<1.3	436		
31A	132.15	6.36	1.00	3195.7	<0.5	<1	30.57	10.95	<5		20329	<6	194.5	70	<31.8	<3.2			
32D	134.25	11.80	0.84	811.76	1.16	<1	9.94	6.86	<5		9577	<12	117.3	81	<59.0	13.7			
32A	135.80	5.79	1.00	2775.7	<0.2	12.86	26.98	14.88	<1	38	16064	74.43	156.1	86	<5.8	<1.2	221		
33G	137.65	6.43	1.00	2733.6	<0.2	9.34	26.41	10.33	<1	72	17588	60.09	169.9	66	<6.4	<1.3	462		
33B	140.15	6.45	1.00	2738.1	<0.2	13.15	25.44	11.05	<1	34	17672	84.87	164.2	71	<6.5	<1.3	219		
35K	141.05	8.72	1.00	2593.9	<0.2	8.51	23.87	8.49	<1	43	22623	74.22	208.2	74	<8.7	<1.7	376		
35C	144.85	6.15	1.00	1552.5	<0.2	2.01	15.77	10.75	<1	134	9550	12.36	97.0	66	<6.2	<1.2	826		
35A	145.85	3.89	1.00	2454.2	<0.2	4.16	26.28	12.40	8.12	41	9544	16.18	102.2	48	<31.6	<0.8	160		
36D	147.45	10.20	1.00	761.89	0.75	<1	9.86	7.66	<5		7774	<10	100.6	78	<51.0	7.7			
36B	148.45	4.35	1.00	1385.4	<0.2	0.78	17.42	19.82	<1	39	6033	3.40	75.9	86	<4.4	<0.9	171		
37D	149.65	7.72	1.00	2140	<0.2	2.32	21.31	11.87	<1	59	16524	17.91	164.5	92	<7.7	<1.5	452		
38G	152.10	4.32	1.00	408.97	1.28	<1	11.33	17.88	<5		1768	<4	40.0	77	<1.6	<5			
38E	153.10	7.11	1.00	241.57	<2	<0.04	7.39	17.71	0.22	60	1718	<0.28	52.6	126	<1.6				

Table B.9. Anion Content of Water Extracts of Borehole 299-W23-19 Sediments (3 Sheets)

Sample ID	Depth (ft bgs)	Dilution Factor	Water:Soil Ratio	1:1 Extracts (mg/L)						Dilution Corrected Porewater (mg/L)							
				Nitrate	Fluoride	Nitrite	Chloride	Sulfate	Phosphate	Alk*	Nitrate	Nitrite	Chloride	Sulfate	Phosphate	Fluoride	Alk*
38E-DUP	153.10	7.11	1.00	216.81	<2	<0.04	6.91	14.34	0.18		1543	<0.28	49.2	102	<1.3	<14	
39D	155.35	9.49	0.82	292.81	0.31	<0.1	7.61	14.22	<0.5		2779	<0.9	72.2	135	<4.7	2.9	
39C	155.85	12.83	1.00	90.08	0.30	<0.04	3.81	11.03	<1	76	1156	<0.51	48.9	142	<12.8	3.85	971
39C-dup	155.85	12.82	1.00	83.59	0.30	<0.04	3.59	11.25	<1		1072	<0.51	46.0	144	<12.8	12.82	
40B	157.75	20.49	1.00	3.56	0.32	<0.04	1.34	5.98	<0.1		73	<0.82	27.5	123	<2.0	6.56	
40	158.65	10.96	1.38	24.93	0.56	<0.1	2.12	38.84	<0.5	74	273	<1.1	23.2	426	<5.5	6.1	815
17SK	159.75	11.92	1.00	32.24	0.84	<0.1	4.25	14.47	<0.5		384	<1.2	50.7	173	<6.0	10.0	
18SKA	161	14.68	1.01	23.02	2.3	<0.1	3.03	17.31	<5		338	<1.5	44.5	254	<73.4	33.8	
18SKB	161.00	19.78	1.04	28.29	<0.1	2.72	0.94	16.99	<0.5		560	54	18.6	336	<9.9	<2.0	
18SKC	166.50	34.13	1.01	17.19	<0.1	3.75	1	12.96	<0.5		587	128	34.1	442	<17.1	<3.4	
19SKA	166.50	74.25	1.00	11.36	1.01	<0.1	1.6	10.29	<0.5		843	<7.4	118.8	764	<37.1	75.0	
19SKB	176.00	80.64	1.00	5.65	0.44	<0.1	1.27	11.28	<0.5		456	<8.1	102.4	910	<40.3	35.5	
41A	184.45	25.37	1.00	6.53	0.37	<0.04	1.28	5.17	<0.1	440	166	<1.01	32.5	131	<2.5	9.4	11170
19SKC	185	114.65	1.01	3.87	0.42	<0.1	1.36	6.5	<0.5		444	<11.5	155.9	745	<57.3	48.2	
20SKA	185	78.06	1.00	0.78	0.65	<0.1	1.45	4.13	<0.5		61	<7.8	113.2	322	<39.0	50.7	
20SKB	189.5	82.45	0.94	3.13	0.58	<0.1	2.51	5.09	<0.5		258	<8.2	206.9	420	<41.2	47.8	
42	194.55	17.10	1.00	1.14	0.65	<0.04	2.00	7.38	<0.1	57	19	<0.68	34.2	126	<1.7	11.1	966
43B	204.50	16.25	1.00	76.79	0.36	<0.04	3.59	7.68	0.13	45	1248	<0.65	58.3	125	<2.1	5.85	736
43A	205.15	41.39	1.00	25.29	0.53	<0.1	1.47	3.68	<0.5		1047	<4.1	60.8	152	<20.7	21.9	

Note: Values in *italics* represent water extracts that were inadvertently run at a ratio of less than 1:1 and analytes reported may be biased high in relationship to the correct 1:1 extract samples. Values in bold represent water extracts that were inadvertently run at a ratio greater than 1:1 and analytes reported may be biased low in relationship to the correct 1:1 extract samples.

*Alk = alkalinity as mg/L of CaCO₃; alkalinity values in bold red type are anomalous. Auto-Titrator was acting up.
 ND = not determined; blank cells also represent analytes not determined/measured.

Figure B.14. Anions Calculated and Actual Porewaters
for Borehole 299-W23-19 Sediments

Water extract cation concentrations as a function of depth are listed in Table B.10 and graphed in Figure B.15. Among the cations, elevated sodium concentrations are the primary tank SX-115 fluid indicator. Maximum values begin abruptly at 22 m (73 ft) bgs, remain elevated above 1000mg/L until 38 m (126 ft) bgs, and gradually decrease. The lower edge of the sodium zone is blurred (approximately 43 to 46 m [143 to 150 ft] bgs). Calcium, magnesium, potassium, and natural strontium show elevated concentrations between 35 and 46 m (116 and 150 ft) bgs, a depth range slightly lower *than* the sodium range. The relative positioning of sodium concentration ranges versus that of the other cations supports the hypothesis that sodium preferentially replaces these cations in sorption sites as it migrates vertically and pushes them ahead to the leading edge of the plume.

A small secondary elevated sodium concentration depth interval occurs in the Ringold Formation between 51 and 58 m (166 and 190 ft) bgs, approximately the same location as the secondary elevated sulfate and chloride concentrations. Calcium, potassium, and iron are also slightly elevated, once again suggesting that residual constituents from fluids that created the high water table in the 1980s were left behind in the soil column after drainage.

The last group of constituents analyzed included radionuclides and trace metals. Of these only technetium-99 and chromium are clearly present in concentrations above background and are attributed to have originated in the tank SX-115 fluid. Water extract concentrations are listed in Table B.11, and technetium-99 distribution is shown in Figure B.16. The technetium-99 elevated concentration pattern closely mimics the nitrate concentration distribution where clearly elevated concentrations begin at 22 m (73 ft) bgs and reaches maximum concentrations of approximately 1,100 to 3,000 pCi/L between 38 and 46 m (125 and 150 ft) bgs. Another sharp drop occurs at 49 m (160 ft) bgs, at the contact between subunit PPlc and the Ringold Formation. Chromium concentration values increase above background beginning at 20 m (67 ft) bgs and reach maximum concentrations of 42,000 to 122,000 µg/L between 22 and 38 m (73 and 125 ft) bgs. The occurrence of the maximum chromium range high in the soil column relative to technetium-99 indicates some retarding chemical mechanism has slowed chromium migration relative to technetium-99. Work completed by the S&T activity (Appendix D, Section D.4.1) indicates that iron(II)-rich minerals in the vadose zone soil reduce the oxidation state of a fraction of the chromium in solution from +6 to +3. In the +3 state, chromium is removed from solution by sorption or coprecipitation in iron(II)-rich minerals.

Trace constituents of other radionuclides are present in the soil column including cesium-137, uranium, and tritium. Cesium-137 occurs at concentrations of approximately 0.1 to 0.6 pCi/g between 20 and 23 m (67 and 74 ft) bgs and may be derived from the tank SX-115 leak. If so, the depth interval marks the approximate location of initial tank fluid occurrence at this location. Uranium occurs at background level and tritium, whose concentration levels are low and occur in the Plio-Pleistocene unit, is of uncertain origin.

B.3.4 CONTAMINANT CONCENTRATIONS

Contaminant concentrations at borehole 299-W23-19 were not analyzed.

**Table B.10. Calculated Porewater Cation Composition from Water Extracts from
Vadose Zone Sediments from Borehole 299-W23-19 (4 Sheets)**

Sample ID	Depth (ft bgs)	Dilution Factor	Water:Soil Ratio	Aluminum (µg/L)	Barium (µg/L)	Calcium (mg/L)	Iron (µg/L)	Potassium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Silicon (mg/L)	Strontium (µg/L)	Sulfate (mg/L)	Manganese (µg/L)
09E	32.95	9.85	1.00	341	248	66	335	44	12	185	189	380	19	10
15A	54.50	17.13	1.00	327	153	134	1097	105	27	611	277	319	226	73
16A	57.45	15.82	1.00	51	197	143	680	79	30	432	253	186	266	38
17J	61.75	18.84	1.00	548	170	101	1093	60	21	359	237	297	163	41
17G	63.25	11.13	1.00	85	156	71	746	32	14	250	172	142	132	21
17F	63.75	8.53	1.00	211	85	65	1416	25	13	243	154	135	125	32
17F-dup	64.75	8.56	1.01	317	101	63	592	25	12	215	159	375	105	11
17DE-aft	64.75	10.70	0.96	164	161	72	308	27	14	316	198	123	126	12
17DE	64.75	5.05	1.00	<250	65	62	71	19	8	164	94	315	157	2
17C	65.25	9.03	1.00	<250	144	77	824	29	15	231	150	123	178	22
18I	67.45	5.74	1.00	2045	103	62	4160	19	12	163	103	154	146	64
18E	69.45	10.19	1.00	182	81	36	526	26	6	373	168	205	126	16
18CB	70.70	6.56	1.00	1882	72	8	4559	11	1	537	119	206	134	84
18CB-dup	70.70	6.56	1.00	2896	90	10	7919	14	2	518	124	54	147	140
19H	73.25	21.10	1.00	3057	692	25	5361	39	3	3081	372	192	458	131
19G	73.75	7.49	0.86	<250	112	18	1477	23	2	1632	112	130	311	54
19E	74.75	7.09	1.00	442	92	17	2543	21	2	1542	113	36	321	96
19D	75.25	9.61	1.18	1554	154	12	3340	22	1	1825	148	98	273	67
20F	79.25	9.47	0.76	529	332	10	1694	25	1	1977	148	86	301	39
20F-dup	79.25	9.38	1.04	1267	910	12	5357	23	1	1841	156	122	265	126
20E	79.75	7.79	1.00	1166	156	9	9829	19	1	1472	125	74	214	146
20D	80.25	6.00	1.00	1210	78	6	6094	15	1	1365	97	2998	219	115
21A	86.00	13.58	0.61	2555	693	10	2660	24	2	2046	254	106	190	76
22D	88.10	6.07	1.00	490	103	7	3413	18	1	1476	63	3033	261	85

**Table B.10. Calculated Porewater Cation Composition from Water Extracts from
Vadose Zone Sediments from Borehole 299-W23-19 (4 Sheets)**

Sample ID	Depth (ft bgs)	Dilution Factor	Water:Soil Ratio	Aluminum (µg/L)	Barium (µg/L)	Calcium (mg/L)	Iron (µg/L)	Potassium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Silicon (mg/L)	Strontium (µg/L)	Sulfate (mg/L)	Manganese (µg/L)
24A	95.00	10.82	1.00	2038	141	17	3773	28	3	1921	103	140	378	61
25B	99.06	14.17	0.81	747	935	29	365	35	4	1781	148	210	468	11
25B-dup	99.06	15.85	0.97	888	206	19	396	31	3	1612	173	128	396	8
25A	100.06	11.40	0.79	811	365	103	899	62	16	2351	134	651	697	13
26E	102.95	13.75	1.00	<1000	289	16	1142	26	2	1589	127	129	454	39
26A	104.95	12.21	1.00	890	281	9	448	18	1	1360	111	74	322	18
27G	107.05	15.02	1.00	<1000	210	162	480	57	32	2457	181	509	570	12
29D	116.35	13.67	1.00	374	670	844	107	128	158	1619	191	4116	511	52
30G	123.85	11.13	1.00	<500	1157	1670	23	170	338	1481	122	8332	798	428
30D	125.35	6.78	0.79	<500	705	2653	30	142	518	1111	74	12930	587	296
30B	126.35	6.03	1.00	<500	1575	3906	1773	112	749	1289	67	20317	249	818
30B-dup	126.35	6.03	1.00	<500	1730	4349	48	122	835	1414	71	23461	268	832
31G-1st	129.15	6.62	1.00	<500	7202	5618	<50	129	1150	818	71	35522	93	883
31G	129.15	5.15	1.00	<500	7549	5000	12	142	999	680	51	30836	82	728
31A	132.15	6.36	1.00	<500	6285	3740	63	147	892	655	71	23715	71	335
31A	132.15	6.35	1.00	<500	5493	3522	28	132	819	589	66	22157	55	301
32D	134.25	11.80	0.84	<500	2560	1788	88	128	472	513	127	9996	77	70
32A	135.80	5.79	1.00	<500	5168	3374	1	100	823	534	60	19626	69	250
33G	137.65	6.43	1.00	<500	5044	3578	<50	104	893	523	64	20064	65	306
33B	140.15	6.45	1.00	<500	5486	3498	6	111	876	528	65	21405	75	253
35K	"141.05"	8.72	1.00	<500	7003	4552	35	139	1191	689	88	26880	84	450
35H-alt	141.85	6.50	1.00	<500	4275	2885	151	89	817	533	64	17040	73	30
35F-alt	143.35	7.18	1.04	<500	3275	2361	151	82	723	478	74	13667	87	28
35C	144.85	6.15	1.00	<500	2805	1743	18	81	521	391	55	9738	73	134

**Table B.10. Calculated Porewater Cation Composition from Water Extracts from
Vadose Zone Sediments from Borehole 299-W23-19 (4 Sheets)**

Sample ID	Depth (ft bgs)	Dilution Factor	Water:Soil Ratio	Aluminum (µg/L)	Barium (µg/L)	Calcium (mg/L)	Iron (µg/L)	Potassium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Silicon (mg/L)	Strontium (µg/L)	Sulfate (mg/L)	Manganese (µg/L)
35A	145.85	3.89	1.00	<500	2921	1811	16	57	554	412	43	10833	55	9
36D	147.45	10.20	1.00	<500	2959	1388	81	106	476	430	85	8160	76	29
36B	148.45	4.35	1.00	<500	1859	1047	30	56	377	341	47	6238	71	6
37D	149.03	1.12	1.00	<500	3891	3086	<20	150	873	554	74	17468	95	2496
38G	152.10	4.32	1.00	<500	661	282	25	36	122	192	48	1753	80	2
38G	152.10	4.32	1.00	<500	709	300	55	37	129	175	47	1845	76	3
38E	153.10	7.11	1.00	93	783	268	138	49	124	257	70	1472	100	8
38E-dup	153.10	7.11	1.00	162	665	252	25	53	117	237	72	1454	95	27
38A-aft	155.10	10.92	1.00	<500	448	152	680	50	74	242	162	513	151	30
39D	155.35	9.49	0.82	<500	2743	526	97	91	226	352	111	3365	179	66
39C	155.85	12.83	1.00	151	706	250	285	75	122	318	222	1231	139	9
39C-dup	155.85	12.82	1.00	<500	554	237	<50	66	115	309	206	1088	131	12
40B	157.75	20.49	1.00	156	451	218	746	79	104	328	323	1210	126	30
40	158.65	10.96	1.38	<500	932	210	65	66	92	226	189	1268	471	6
17SK	159.75	11.92	1.00	<500	596	170	89	65	67	273	195	1083	188	45
18SKA	161	14.68	1.01	<500	822	180	46	74	66	317	222	1088	267	45
18SKB	161.00	19.78	1.04	<500	1009	235	170	97	90	392	278	1371	368	62
18SKC	166.50	34.13	1.01	<500	1843	157	222	118	42	483	239	1018	480	22
19SKA	166.50	74.25	1.00	<500	1336	343	379	209	62	857	626	2036	821	29
19SKB	176.00	80.64	1.00	<500	887	372	419	223	56	904	814	1870	878	79
41A	184.45	25.37	1.00	297	127	76	1091	55	24	213	274	845	128	37
19SKC	185	114.65	1.01	<500	1605	315	757	235	87	965	951	1873	796	83
20SKA	185	78.06	1.00	<500	1952	294	1226	211	74	776	606	1558	342	310
20SKB	189.5	82.45	0.94	<500	1154	308	618	223	83	877	700	1772	501	379

**Table B.10. Calculated Porewater Cation Composition from Water Extracts from
Vadose Zone Sediments from Borehole 299-W23-19 (4 Sheets)**

Sample ID	Depth (ft bgs)	Dilution Factor	Water:Soil Ratio	Aluminum (µg/L)	Barium (µg/L)	Calcium (mg/L)	Iron (µg/L)	Potassium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Silicon (mg/L)	Strontium (µg/L)	Sulfate (mg/L)	Manganese (µg/L)
42	194.55	17.10	1.00	15095	257	109	15152	61	39	250	245	990	144	394
43B	204.50	16.25	1.00	421	487	280	487	72	91	267	156	1268	120	123
43A	205.15	41.39	1.00	<500	2691	173	435	101	30	411	421	1064	214	28

Notes: Extracts with incorrect water to sediment ratios are in bold. Note that some analytes are reported as µg/L and others mg/L.

alt = water extract AFTER Ultracentrifugation to remove actual porewater.

dup = a duplicate water extract on a separate aliquot of sediment.

SK# = sediment from air rotary sock not from core barrel.

Figure B.15. Cations Calculated and Actual Porewaters for Borehole 299-W23-19 Sediments

**Table B.11. Calculated Porewater Trace Metal Composition for Water
Extracts of Sediments from Borehole 299-W23-19 (3 Sheets)**

Sample ID	Depth (ft bgs)	Dilution Factor	Water:Soil Ratio	Technetium-99 (pCi/mL)	U	Cr	As	Se	Mo	Ag	Cd	Pb
					(µg/L)							
09E	32.95	9.85	1.00	<8	11.7	<25	244	<25	87	<1	<1.0	7.4
15A	54.50	17.13	1.00	<15	19.4	<9	131	<43	149	<4	<4.3	<286
16A	57.45	15.82	1.00	<13	15.7	<8	162	<40	191	<4	<4.0	39.6
17J	61.75	18.84	1.00	<16	20.2	9.6	248	<47	93	<5	<4.7	244.8
17G	63.25	11.13	1.00	<9	14.2	<6	213	<28	62	<3	<2.8	<28
17F	63.75	8.53	1.00	<7	12.9	12.2	185	<21	45	<2	<2.1	<21
17F-dup	64.75	8.56	1.01	<7	13.2	<4	187	<21	44	<2	<2.1	<21
17DE	64.75	5.05	1.00	<2	5.5	8.1	103	6.3	60	<1	<0.2	0.8
17DE-aft	64.75	10.70	0.96	<9	12.4	5.3	327	<27	91	<3	a. 7	<26.75
17C	65.25	9.03	1.00	<8	9.5	<4.5	185	<23	115	<2	<36.1	<23
18I	67.45	5.74	1.00	<5	5.6	96	135	<14	49	<1	<1.4	19.7
18E	69.45	10.19	1.00	<9	9.0	308	190	<25	147	<1	<1.0	6.9
18C	70.45	6.56	1.00	<6	15.6	3224	273	<16	152	0.9	<0.7	6.3
18B	70.95	6.56	1.00	<6	15.6	3343	268	<16	154	1.0	3.9	8.4
19H	73.25	27.70	1.00	357.0	55.1	43262	1175	34	1352	7.5	2.2	15.2
19G	73.75	7.49	0.86	312.4	23.1	37442	681	34	1179	7.1	1.8	12.1
19E	74.75	7.09	1.00	333.9	23.6	48547	617	22	1028	6.1	1.0	8.1
19D	75.25	9.61	1.18	317.7	32.7	30391	2266	26	656	3.9	1.4	7.2
20F	79.25	9.47	0.76	284.4	45.4	35668	2630	26	1412	4.0	2.0	7.1
20F-dup	79.25	9.38	1.04	245.8	41.2	29695	2345	18	1090	3.4	1.6	16.6
20E	79.75	7.79	1.00	198.2	20.7	21235	3463	22	667	4.1	1.4	34.8
20D	80.25	6.00	1.00	192.4	15.6	19834	2433	20	523	1.5	1.5	15.0
21A	86.00	13.58	0.61	94.4	62.3	5422	2229	20	310	1.0	0.8	4.1
22D	88.10	6.07	1.00	288.9	51.6	39232	616	17	731	3.7	0.8	10.0
24A	95.00	10.82	1.00	330.9	26.0	40792	1063	24	3850	4.4	2.7	17.0
25B	99.06	14.17	0.81	120.2	19.7	27723	868	27	164	0.4	0.9	6.2
25B-dup	99.06	15.85	0.97	122.3	20.7	28227	1099	18	144	0.5	0.6	2.3
25A	100.06	11.40	0.79	394.5	13.1	85566	466	45			0.8	
26E	102.95	13.75	1.00	177.2	36.3	35900	1146	18	3495	2.0	4.3	9.6
26A	104.95	12.21	1.00	155.3	33.2	16064	801	18	3288	0.0	3.7	6.9
27G	107.05	15.02	1.00	545.7	14.7	122342	291	38	1875	3.8	3.8	37.6

Sample ID	Depth (ft bgs)	Dilution Factor	Water:Soil Ratio	Technetium-99 (pCi/mL)	U	Cr	As	Se	Mo	Ag	Cd	Pb
29D	116.35	13.67	1.00	506.2	14.1	93333	70	50	137	3.4	3.4	34.2
						81170	33	73	332	0.6	1.3	2.5
30D	125.35	6.78	0.79	1504.7	6.6	42511	34	123	129	2.0	0.9	2.2
30B	126.35	6.03	1.00	2034.1	6.5	1788	7.1	139	108	4.0	1.5	28.2
30B-dup	126.35	6.03	1.00	2344.4	7.1	2584	6.5	144	101	4.2	1.5	15.1
31G	129.15	6.62	1.00	3291.0	9.1	18	4.6	102	81	2.0	1.1	4.1
31G	129.15	5.15	1.00	3033.6	3.3	31	20	73	57	1.1	0.7	1.9
31A	132.15	6.36	1.00	2498.7	4.0	0.01	15	45	50	1.4	0.8	1.1
31A	132.15	6.35	1.00	2457.2	4.2	6.4	15	43	49	1.3	0.7	3.4
32D	134.25	11.80	0.84	1169.5	6.7	4.7	33	40	134	0.0	0.5	2.0
32A	135.80	5.79	1.00	2109.7	8.2	<14	2.9	68	67	1.9	0.7	<3
33G	137.65	6.43	1.00	2235.4	8.2	<16	<3	78	71	1.6	1.0	<3
33B	140.15	6.45	1.00	2117.2	10.3	<16	<3	79	104	2.3	0.9	<3
35K	"141.05"	8.72	1.00	2204.1	18.5	c22	5.0		164	1.4	1.2	
35IH-aft	141.85	6.30	1.00	1772.9	9.4	6.6	5.4			1.6	<1.6	<16
35F-aft	143.35	7.18	1.04	1613.3	10.5	5.9	6.5	49	100	<2	<1.8	<18
35C	144.85	6.15	1.00	1138.1	7.0	<15	6.5	28	121	<1	<0.6	<3
						3.7	4.1	29	48	<1	<1.0	<10
36D	147.45	10.20	1.00	1170.7	7.4	3.6	18	23	141	<1	0.6	3.4
36B	148.45	4.35	1.00	831.2	8.4	6.5	5.8	22	74	<1	<1.1	<11
						<19	4.0	50	208	<1	<2.1	<4
38G	152.10	4.32	1.00	237.3	7.6	4.3	19	18	83	<0	0.2	0.8
38G	152.10	4.32	1.00	249.6	7.7	3.8	20	18	88	<0	0.2	0.6
38E	153.10	7.11	1.00	152.8	12.2	5.2	43	24	147	<2	<1.8	<18
38E-dup	153.10	7.11	1.00	142.8	12.0	4.4	44	20	156	<2	<1.8	<18
38A-aft	155.10	10.92	1.00	37.3	20.1	<5	391	<27	157	<3	<2.7	<27
39D	155.35	9.49	0.82	293.2	36.1	9.9	28	21	309	<1	0.8	12
39C	155.85	12.83	1.00	138.6	36.1	<32	510	<32	160	<1	<1.3	<6
						<32	483			<1	<1.3	<6
40B	157.75	20.49	1.00	23.3	99.1	10.4	448	<32	165	<5	<5.1	51.2
						11.2	194	32	226	<1	0.9	2.9

**Table B.II. Calculated Porewater Trace Metal Composition for Water
Extracts of Sediments from Borehole 299-W23-19 (3 Sheets)**

Sample ID	Depth (ft bgs)	Dilution Factor	Water:Soil Ratio	Technetium-99 (pCi/mL)	U	Cr	As	Se	Mo	Ag	Cd	Pb
					(µg/L)							
17SK	159.75	11.92	1.00	30.7	25.3	64.6	276	30	886	<1	1.3	1.4
18SKA	161	14.68	1.01	23.6	20.0	42.9	332	27	1276	<1	2.1	8.4
18SKB	161.00	19.78	1.04	52.3	28.7	83.4	388	34	1417	<2	2.5	2.4
18SKC	166.50	34.13	1.01	53.8	3.5	41.8	12	24	1157	<3	2.1	6.3
19SKB	176.00	80.64	1.00	45.1	11.6	19.0	115	54	1524	<8	4.0	26.1
41A	184.45	25.37	1.00	13.1	9.5	14.1	94	<63	384	<6	<6.3	<63
19SKC	185	114.65	1.01	31.1	12.6	<115	145	83	2368	<11	4.6	8.7
20SKA	185	78.06	1.00	14.6	19.8	0.0	191	47	1212	<8	4.2	33.7
20SKB	189.5	82.45	0.94	25.2	12.2	12.9	205	89	1887	<8	4.0	13.9
42	194.55	17.10	1.00	5.6	34.2	9.2	50	42	279	<4	<4.3	<43
43B	204.50	16.25	1.00	51.1	25.0	<8	23	<41	247	<4	<4.1	47.4

**Figure B.16. Trace Metals Calculated from Sediment Water Extracts
and Actual Porewaters for 299-W23-19 Sediment**

B.3.5 CHEMICAL INTERACTIONS

No specific experiments were completed on soils from this borehole to quantify geochemical reactions influencing contaminant migration. Dominant chemical reactions affecting radionuclides and tank fluid chemicals are inferred from the relative location of these constituents in the soil column, comparison of acid-leachable versus water-leachable concentrations for specific contaminants, and general knowledge of the tank fluid chemistry. Greater contaminant mobility is inferred from the occurrence of high concentration zones deeper in the vadose zone and smaller differences in concentrations leached by water versus acid.

Generally speaking, the data suggest that tank SX-115 fluid chemistry, other than providing increased amounts of certain constituents to the soil column, had little effect on the chemical behavior of contaminants in the sense that chemical reactions between tank fluid constituents and the soil column environment were largely controlled by soil-soil water reactions. Constituent anions (e.g., nitrate and technetium-99) have migrated the most rapidly and mark the leading edge of vertical tank fluid migration at this location. Chromium was slightly retarded relative to technetium-99 and nitrate, presumably because of oxidation reduction, allowing fixation on soil. Constituent cations have migrated varying distances depending on the strength of retardation mechanisms. Cesium-137 sorbed very strongly as soon as tank fluid entered the soil column. Sodium concentrations, being relatively high, successfully completed for sorption sites in vadose zone soils, were somewhat retarded. Calcium, magnesium, and indigenous strontium were displaced by sodium and pushed ahead of sodium during migration.

B.3.6 GROUNDWATER MEASUREMENTS

Groundwater contaminants in this borehole are characterized by the largest technetium-99 concentrations currently seen in the monitoring network. Recent analyses are listed in Appendix C, Table C.17. Also, nitrate and chromium concentrations are high. The technetium-99/nitrate ratios ($0.11 \text{ pCi}/\mu\text{g}$) are similar to those postulated for tank fluids. This observation, coupled with the location of borehole 299-W23-19 strongly indicates the tank SX-115 leak as the source of this groundwater contamination.

B.4.0 TANK SX-108 *SLANT* BOREHOLE

This section summarizes data reported in *Geologic and Geochemical Data Collected from Vadose Zone Sediments from Slant Borehole [SX-108] in the S/SX Waste Management Area and Preliminary Interpretations* (Seme et al. 2001d) except for the groundwater sample data, which are reported in the WMA S-SX RCRA groundwater monitoring report (Johnson and Chou 2000). The SX-108 slant borehole was completed to further characterize the nature and extent of vadose zone contaminants supplied by a tank SX-108 leak. This borehole was drilled specifically to sample soils as close the tank leak site as possible and to investigate tank fluid migration underneath the tank, an area which has received no evaluation other than gross gamma measurements along laterals in the 1970s. Soils analyses from the slant borehole combined with analyses from borehole 41-09-39 provides a means of comparing tank fluid migration in two different locations with somewhat different conditions occurring. In addition to being closer to the tank leak, the slant borehole goes through the 'umbrella' region under the tank where little if any natural infiltration is anticipated, compared to the region between the tanks. Also, the addition of second borehole data provides a better idea of the three-dimensional aspect of the migrating leak distribution.

The most significant data provided by this characterization effort were soil measurements of radionuclides and chemicals attributed to this leak. Elevated concentrations of several constituents were measured in soils throughout the length of the slant borehole from 17 and 41 m (55 and 135 ft) bgs. This depth interval includes subunits H1 and H2 of the Hanford formation and part of subunit PPlz) of the Plio-Pleistocene unit. The primary radionuclides present in this zone are cesium-137 and technetium-99. Maximum cesium-137 concentrations are present between 17 and 27 m (55 and 88 ft) bgs in subunit H1 and the top part of subunit H2. Maximum technetium-99 concentrations are present in the bottom part subunit H2 and the top part of subunit PPlz between 26 and 42 m (85 and 138 ft) bgs. The primary chemical characteristics attributed to tank fluid-soil interaction within this zone are elevated pH, sodium, chromium, and nitrate. The depth of maximum technetium-99 concentration coincides with high nitrate concentrations and marks the leading edge of vertical tank fluid migration at this location. Also, this is the only borehole in which iodine-129 has been detected. Iodine-129 occurs between 24 and 40 m (80 and 130 ft) bgs at about 18,000 to 43,000 pCi/L.

It is of note that most constituents show more than one peak concentration with depth within their respective highest concentration ranges. Several mechanisms may have played a role in creating these patterns of contaminant concentration, including stratigraphic heterogeneities that encourage layering, thermal cycling effects that temporarily created circulating fluids in the soil column, and/or multiple leaks. None of these various options are clearly preferred.

Moisture content measurements are somewhat dry and in situ temperatures are elevated relative to undisturbed Hanford formation soils. Both conditions plus the presence of the tank suggest that relatively little drainage is occurring in this area. The lack of tank fluid contaminants below the Plio-Pleistocene unit and the low concentrations of technetium-99 and nitrate in groundwater samples from nearby borehole 41-09-39 indicate that contaminants from this area have not reached the unconfined aquifer at this location.

B.4.1 GEOLOGY

The SX-108 slant borehole intersected three primary stratigraphic units: (1) backfill, which was not sampled, (2) the Hanford formation, and (3) the top of the Plio-Pleistocene unit. The backfill appears to extend to about 16.2 m (53 ft) bgs where it contacts the Hanford formation. The next 2.6 m (8 ft) bgs is interpreted to correlate with the upper fine sand and mud sequence of the Hanford formation subunit H1a. Below this lies the 4.2 m (14 ft) thick middle coarse sand and gravel sequence of subunit H1. The contact between the Hanford formation and the Plio-Pleistocene unit is interpreted to occur at 38.5 m (126 ft) bgs. The frequency and manner in which the samples were taken limits the completeness of the geologic description that can be made.

B.4.1.1 Backfill

The backfill was not sampled. The contact depth of the backfill with the Hanford formation at 16.2 m (53.1 ft) bgs is supported by tank farm engineering drawings (H-2-37985 sheet 2 of 2), an increase in blow counts required to advance the casing, and an increase in apparent moisture content as indicated in the neutron moisture log.

B.4.1.2 Hanford formation

All three Hanford formation subunits (H1a, H1, and H2) were present at the SX-108 slant borehole and sampled.

- **Subunit H1a** – This subunit, the upper fine sand and mud sequence, is believed to be approximately 2.6 m (8.4 ft) thick extending from the base of the backfill to a vertical depth of approximately 18.7 m (61.5 ft) bgs. The location of *this* contact is supported by a slight increase in the blow counts and a sharp decrease in the neutron-neutron moisture log response. Layering was evident in the single sample retrieved from subunit H1a. From 16.6 to 16.9 m (54.5 to 55.3 ft) bgs the sample exhibited a layer of dry gray muddy (silty) sand containing some possible rock flour, overlying a moist muddy, medium sand.
- **Subunit H1** – This subunit, the middle coarse sand and gravel sequence, is estimated to be approximately 4.2 m (13.8 ft) thick extending to a vertical depth of approximately 22.9 m (75.3 ft) bgs. The depth to this contact is supported by a sharp decrease in blow counts and an increase in the neutron-neutron moisture log response. The moisture log response is further substantiated by an increase in gravimetric moisture content below the contact. Two samples were recovered from subunit H1. One sample was lost. The recovered samples show some coarse layering. Sample S0070-03 was described as a dry grayish-brown medium to fine sand with some mud and gravel fragments (up to medium pebble). Sample S0070-04 contained some fine gray powder (rock flour) and the remainder of the sample was a salt and pepper textured medium to fine sand; no gravel was noted.
- **Subunit H2** – This subunit, the lower fine sand and mud sequence, is estimated to be about 15.6 m (51.1 ft) thick, extending to a vertical depth of approximately 38.5 m (126.4 ft) bgs. This depth is supported by a slight increase in the blow counts and a sharp increase in the neutron-neutron moisture log response. There is a parallel increase in

gravimetric moisture content of the samples below the contact. Ten split-spoon samples were collected through this horizon between 22.9 and 38.5 m (75.3 to 126.4 ft) bgs. Subunit H2 is composed of stratified sand, muddy sand and mud. The laminar nature of this unit is one of its outstanding characteristics. Thin laminations of mud and sand commonly separate the sand strata.

B.4.1.3 Plio-Pleistocene Unit

The Plio-Pleistocene unit was penetrated but its lower contact was not encountered in the slant borehole. Three split-spoon samples were collected from this horizon. The unit is composed of interstratified mud and muddy, very fine sand with occasional very fine sand strata (i.e., PPlz subunit). The sandier strata were described as friable and frequently exhibiting finely laminated muds.

B.4.2 GEOPHYSICAL AND PHYSICAL PROPERTY MEASUREMENTS

Several geophysical logging techniques were used during and after installation of the SX-108 slant borehole. These techniques included the following:

- Gyroscopic borehole surveys
- Casing wall temperature logging using an infrared sensor
- Neutron-neutron moisture logging
- High-purity germanium spectral gamma logging
- High-rate gamma logging.

A composite of the temperature, moisture, spectral gamma, and high-rate gamma logs (Gardner and Reynolds 2000) is shown in Figure B. 17.

The neutron-neutron moisture log recorded the average volumetric moisture content within a 20 to 30 cm (8 to 12 in.) radius. A slightly increased moisture content ~~was~~ noted between vertical depths of 15 and 18 m (50 and 60 ft) bgs, and second significant moisture content change noted at 33 m (107 ft) bgs. These moisture content changes correlate well with changes in the geologic materials.

Several spectral-gamma and high-rate gamma logging events were conducted using different logging systems, shielding configurations, and counting times. Cesium-137 was the only gamma-emitting contaminant detected. Above 16 m (52 ft) bgs, cesium-137 concentrations were generally less than 20 pCi/g, and were attributed (most likely) to internal casing contamination (Gardner and Reynolds 2000). This internal casing contamination resulted from the loss of sample S0070-02 down the borehole. Between depths of 16 and 27 m (53 and 90 ft) bgs very high concentrations of cesium-137 (on the order of 10^8 pCi/g) were measured. Internal contamination and/or dragdown most likely dominate contamination detected below 27 m (90 ft) bgs (Gardner and Reynolds 2000).

Figure B.17. Geophysics Logging Graph for SX-108 Slant Borehole

Laboratory measurements of soil moisture content (Table B. 12 and Figure B. 18) show similar trends in relative concentrations as the neutron-neutron moisture measurements. The moisture profile shows one high peak in subunit H2 at a laminated sand facies with a silt tringer at 32 m (105 ft) bgs. With the exception of one sample, the Plio-Pleistocene unit soils show generally the highest moisture content in the soil column.

B.4.3 SOIL WATER CHEMISTRY MEASUREMENTS

In addition to soil physical property measurements (Section B.4.2), an extensive water chemistry analysis has been completed for samples collected at the SX-108 slant borehole between 17 and 44 m (55 and 145 ft) bgs. The primary means of measuring porewater composition was to add deionized water to soil samples to generate enough water for performing analyses. By back-calculating for the dilution introduced by the added water, 'true' concentrations were derived. For a few samples porewater was directly separated from the same soil sample or one nearby and analyzed directly. By comparing the dilution-corrected water extract data with the porewater data in these few samples, an indication of the closeness of the water extract chemistry to original water chemistry was determined. In general, comparisons were not exact but concentration values were generally within a factor of two or better, agreement improved with increasing constituent concentration, and both sets of data showed similar concentrations versus soil depth correlations. Thus, the water extract method is an effective tool for evaluating tank fluid interactions with vadose zone soil.

Water extract pH and electrical conductivity measurements with depth are listed in Table B. 13 and graphed in Figure B.19. Elevated pH values (greater than 9.) are measured between 17 and 25 m (55 and 85 ft) bgs primarily in subunits H1a and H1 and the top part of subunit H2. Because pH values are expected to decrease as increasing interaction with soil and soil water occurs, the location of maximum pH values suggests the approximate initial depth of tank fluid interaction with the vadose zone at this location. As with most chemical indicators at this borehole in the zones of elevated value, an apparent bimodal distribution of pH values is created by the low pH value (8) measured in the middle of the elevated zone at 25 m (80.6 ft) bgs. Increases in electrical conductivity values compared to undisturbed soil water values are also an indicator of tank fluid occurrence in soil. Maximum values of approximately 100,000 to 133,000 $\mu\text{S}/\text{cm}$ are measured between 26 and 30 m (85 and 97 ft) bgs. A secondary range of elevated electrical conductivity values occurs between 35 and 40 m (114 and 130 ft) bgs, primarily at the bottom of subunit H2 and the top of the Plio-Pleistocene subunit PPlz. Maximum electrical conductivity values are an indicator of location for mobile tank fluid constituents and maximum vertical penetration of tank fluids.

**Table B.12. Moisture Content (wt%)
SX-108 Slant Borehole Sediments**

Lithologic Unit	Sample ID	Vertical Depth (ft bgs)	Moisture (%)
H1A	01B	54.5-54.9	ND
H1A	01A	54.9-55.3	4.33
H1	02B	63.0-63.5	NS
H1	02A	63.5-63.7	NS
H1	03B	67.3-67.7	3.76
H1	03A	67.7-68.1	2.76
H1	04B	71.5-71.9	3.55
H1	04A	71.9-72.4	2.77
H2	05B	75.7-76.2	6.48
H2	05A	76.2-76.6	4.69
H2	06B	79.9-80.4	3.50
H2	06A	80.4-80.8	3.68
H2	07B	84.1-84.6	6.60
H2	07A	84.6-85.0	6.18
H2	08B	88.3-88.8	4.52
H2	08A	88.8-89.2	6.02
H2	09B	92.5-92.9	5.32
H2	09A	92.9-93.3	2.35
H2	10B	96.6-97.1	4.62
H2	10A	97.1-97.5	1.91
H2	11B	101.0-101.5	5.50
H2	11A	101.5-101.9	3.15
H2	12B	104.9-105.4	7.02
H2	12A	105.4-105.8	21.35
H2	13B	113.1-113.6	7.95
H2	13A	113.6-114.0	7.64
PPlz	14B	121.3-121.7	8.51
PPlz	14A	121.7-122.2	11.95
PPlz	15B	129.4-129.9	17.50
PPlz	15A	129.9-130.3	17.42
PPlz	16B	137.5-138.0	15.13
PPlz	16A	138.0-138.4	7.50
PPlz	17B	144.0-144.4	14.49
PPlz	17A	144.4-144.9	19.70

ND = not determined.

NS = no sample.

**Figure B.18. Moisture Content (wt%) in Vadose Zone
Sediment Profile at SX-108 Slant Borehole**

Table B.13. Water Extract pX d Electrical Conductivity Values at SX-108 Slant Borehole

Sample ID	Vertical Depth (ft bgs)	Dilution Factor	1:1 pH	1:1 EC (mS/cm)	Pore EC (mS/cm)
01A	55.1	23.13	9.16	0.404	9.34
02A	63.02	NS	NS	NS	NS
03AB	67.9	36.88	9.58	0.701	25.85
04A	72.2	36.15	9.54	0.576	9.57
05A	76.4	21.36	9.78	0.877	14.21
06A	80.6	27.18	8.00	16.71	454.2
07A	84.8	16.20	9.55	54.62	1166.5
08A	89.0	16.61	7.83	49.01	1771.6
09A	93.1	42.56	7.88	31.7±	1009.3
10A	97.3	52.34	8.23	25.56	1337.7
11A	101.7	31.78	8.38	13.93	592.8
12A	105.6	4.69	8.02	2.36	11.04
13A	113.8	13.38	7.99	29.78	398.4
14A	122.0	8.69	7.82	30.24	262.8
15A	130.1	5.74	7.45	40.01	229.7
16A	138.2	13.31	7.24	5.80	77.16
17A	144.6	5.08	7.22	3.47	17.63

EC = electrical conductivity.
 NS = no sample was available.

Figure B.19. SX-108 Slant Borehole pH and Electrical Conductivity Profiles with Depth

Water extract anion concentrations as a function of depth are listed in Table B.14. Nitrate, chloride, and sulfate concentrations with depth are shown in Figure B.20. The primary indicator of tank fluid occurrence is elevated nitrate concentrations, which are measured through the borehole with maximum values between 180,000 and 995,000 mg/L between 25 and 39 m (81 and 130 ft) bgs. An apparent bimodal distribution of nitrate values is created by the low nitrate value (7,191 mg/L) measured in the middle of the elevated zone at 32 m (105.6 ft) bgs. It is probable that the bottom of the nitrate range was not reached in this sampling effort. Elevated levels of chloride (between 26 and 44 m [85 and 145 ft]) and sulfate (between 20 and 39 m [65 and 127 ft]) are also observed. Chloride maximum concentrations (between 27 and 30 m [89 and 130 ft] bgs) and sulfate maximum concentrations between 25 and 40 m (81 and 130 ft) bgs track closely with nitrate in subunit H2 and subunit PPlz. The minimum chlorine and sulfate concentrations (109 and 147 mg/L, respectively) at 32 m (105.6 ft) bgs establishes an apparent bimodal distribution for both anions. Overall, the anion concentrations appear to be diminishing rapidly in the deepest sample and indicate the leading edge of the tank fluid migration near the bottom of the borehole (44 m [145 ft]).

Water extract cation concentrations as a function of depth are listed in Table B.15 and graphed in Figure B.21. Among the cations, elevated sodium concentrations are the primary tank fluid indicator and occur throughout the SX-108 slant borehole. Maximum values begin abruptly at 25 m (81 ft) bgs, remain elevated above 65,000 mg/L through 40 m (130 ft) bgs except at 32 m (105.6 ft) bgs where sodium concentration drops to 691 mg/L. The potassium concentration distribution with depth mimics sodium. Calcium, magnesium, barium, and natural strontium show depleted concentrations above the high sodium depth range at 17 to about 27 m (55 to 90 ft) bgs and elevated concentrations between 27 and 44 m (90 and 145 ft) bgs, a depth range slightly ahead of the high sodium range. The relative positioning of sodium and perhaps potassium concentration ranges versus that of the other cations supports the hypothesis that sodium and potassium preferentially replace these cations in sorption sites as they migrate vertically and push them ahead to the leading edge of the plume.

The last group of constituents analyzed included radionuclides and trace metals. Of these, cesium-137, technetium-99, and chromium are clearly present in concentrations above background and are attributed to have originated in the tank fluid. Gamma log concentrations of cesium-137 are listed in Table B.16 and distribution is shown in Figure B.22.

Above background cesium-137 concentrations are measured throughout the borehole. The primary contamination zone is in subunit H1 and the upper half of subunit H2 between 21 and 27 m (68 and 90 ft) bgs. In this zone two peaks occur at 21 and 24 to 26 m (68 and 80 to 85 ft) bgs at concentration levels of 2×10^7 and 9×10^7 pCi/g. Overall, the vast majority of cesium-137 mass resides in the upper half of subunit H2 between 24 and 26 m (80 and 85 ft) bgs. Just below these peaks, cesium-137 concentrations drop by orders of magnitude (less than 1000 pCi/g at 28 m [93 ft] bgs and below).

Table B.14. Anion Content of Water Extracts of SX-108 Slant Borehole Sediment

Sample ID	Depth (ft bgs)	Dilution Factor	Water:Soil Ratio	ALL IONS (mg/L)						DILUTION CORRECTED FOR WATER (mg/L)							
				Nitrate	Fluoride	Nitrite	Chloride	Sulfate	Phosphate	Alk*	Nitrate	Nitrite	Chloride	Sulfate	Phosphate	Fluoride	Alk*
1A	55.1	23.13	1.00	6.95	1.94	<0.1	1.76	20.0	<0.5	211	161	<2.31	40.7	462	<11.6	44.7	4884
1A-Dup	55.1	23.13	1.00	6.07	1.71	<0.1	1.27	17.5	<0.5	519	140	<2.31	29.4	405	<11.6	39.6	12007
3AB	67.9	36.88	1.02	29.1	3.69	0.36	3.38	21.7	0.87	382	1072	13.1	125	801	0.88	136	14105
4A	72.2	36.15	1.00	23.5	2.27	0.31	1.51	11.5	0.68	387	851	11.2	54.7	415	0.68	81.9	13977
5A	76.4	21.36	1.00	92.9	3.24	0.34	3.92	27.3	1.06	407	1984	7.30	83.8	584	1.06	69.3	8701
6A	80.6	27.18	1.00	11743	ND	ND	<10	70.9	<5	587	319225	ND	<272	1926	<136	ND	15945
7A	84.8	16.20	1.00	46645	<10	ND	26.0	607	<50	1702	755649	ND	421	9833	<810	<162	27577
8A	89.0	16.61	1.00	39713	<10	87.5	83.3	566	<50	886	659796	1453	1383	9412	<831	<166	14725
9A	93.1	42.56	1.00	22852	<10	57.1	123	566	<50	504	972499	2429	5213	24092	<2128	<426	21439
10A	97.3	52.34	1.00	18994	<10	59.0	128	276	<50	484	994113	3088	6713	14465	<2617	<523	25335
11A	101.7	31.78	1.00	9524	<1	<10	130	46.8	<50	130	302677	318	4121	1486	<1589	<31.8	4130
12A	105.6	4.69	1.00	1535	<1	<1	23.3	31.4	<5	100	7191	<46.9	109	147	<23.4	<4.69	467
13A	113.8	13.38	1.02	22223	<10	72.5	213	293	<50	704	297334	970	2846	3923	<669	<134	9418
14A	122.0	8.69	1.04	21496	<10	46.3	187	339	<50	389	186815	402	1624	2945	<435	<86.9	3381
14A-Dup	122.0	8.38	1.00	24084	<10	31.9	212	387	<50	436	201786	267	1773	3246	<419	<83.8	3650
15A	130.1	5.74	1.00	34574	<10	34.4	331	507	<50	541	198485	198	1903	2908	<287	<57.4	3104
16A	138.2	13.31	1.00	4193	<1	<10	56.2	11.4	<5	219	55822	<133	749	151	<66.6	<13.3	2914
17A	144.6	5.08	1.00	2395	<1	<1	34.7	11.6	<5	123	12155	<5.08	176	59.1	<25.4	<5.08	622

*Alk = alkalinity as mg/L of CaCO₃.
 ND = not determined.

**Figure B.20. Anions Calculated and Actual Porewaters
for SX-108 Slant Borehole Sediments**

**Table B.15. Calculated Porewater Cation Composition from Water Extracts
of Vadose Zone Sediments from SX-108 Slant Borehole**

Sample ID	Depth (ft bgs)	Dilution Factor	Water:Soil Ratio	Aluminum (µg/L)	Barium (µg/L)	Calcium (mg/L)	Iron (µg/L)	Potassium (mg/L)	Magnesium (mg/L)	Sodium (mg/L)	Silicon (mg/L)	Strontium (µg/L)	Sulfate (mg/L)	Manganese (µg/L)
1A	55.1	23.13	1.00	16351	(375)	28.23	16197	(77)	(5.7)	2378	420	(259)	451	(585)
1A-Dup	55.1	23.13	1.00	15702	(409)	25.51	14623	(82)	(5.3)	2344	398	<23130	427	(526)
3A	67.9	36.88	1.02	66585	1073	(34.97)	67342	(131)	27.18	6829	734	(265)	855	(1349)
4A	72.2	36.15	1.00	50399	(819)	(32.95)	56108	(86)	(16.9)	7195	865	<36150	526	(882)
5A	76.4	21.36	1.00	26641	(468)	(17.97)	29374	(43)	(4.8)	5716	367	<21360	657	(375)
6A	80.6	27.18	1.00	10769	(223)	1647.9	9997	703	101	153069	(193)	(8131)	2329	<1359
7A	84.8	16.20	1.00	8598	2809	39.59	8481	1339	(3.3)	345472	170.3	(2794)	10402	<810
8A	89.0	16.61	1.00	(3405)	(207)	1966	(3397)	2961	118	305019	(99)	31612	10320	<831
9A	93.1	42.56	1.00	(4924)	(527)	4303	(5271)	4388	151	370034	(225)	45684	22196	<2128
10A	97.3	52.34	1.00	(11869)	1695	1821.3	(12356)	3604	128	391103	(295)	(36890)	13276	<2617
11A	101.7	31.78	1.00	<7945	29778	37905	<7945	1358	3143	65257	(285)	421747	1902	1813
12A	105.6	4.69	1.00	(929)	1739	1309	(929)	87	213	691	66	7485	113	(91)
13A	113.8	13.38	1.02	(2006)	548	1583	(2124)	1001	137	110749	(102)	23332	3600	<669
14A	122.0	8.69	1.04	(1297)	653	1678	(1297)	566	163	68587	(74)	27027	2836	<435
14A-Dup	122.0	8.38	1.00	(1146)	587	1855	(1125)	611	175	73859	(71)	29976	3042	<419
15A	130.1	5.74	1.00	(370)	507	2555	(357)	555	270	70723	82	37277	2891	<287
16A	138.2	13.31	1.00	(577)	18286	10030	(577)	348	2259	4404	164	64992	147	2287
17A	144.6	5.08	1.00	(412)	3519	2169	(412)	113	593	649	60	11816	59	541

Notes: In Sample ID column, Dup represents a duplicate water extract on a separate aliquot of sediment. Note that some analytes are reported as µg/L and others as mg/L. Depth represents the vertical depth in feet; the S values have been converted to sulfate to allow comparison to the anion data in Table 4.4.

**Figure B.21. Cations Calculated and Actual Porewaters
for SX-108 Slant Borehole Sediments**

**Table B.16. Gamma Energy Analysis of Vadose Zone
Sediments at SX-108 Slant Borehole**

Sample ID	Depth (ft bgs)	Cesium-137	± uncertainty	Potassium-40	± uncertainty
		pCi/g		pCi/g	
Hanford Subunit H1a (Sand)					
1A	55.1	3.06E+06	8.55E+04	<3.88E+03	--
Hanford Subunit H1 (Coarse Sand/Gravel)					
3BA	67.9	1.94E+07	5.37E+05	<1.45E+04	--
4B	71.5	8.16E+06	2.27E+05	<7.66E+03	--
4A	72.2	1.38E+06	3.94E+04	<7.21E+03	--
Hanford Subunit H2 (Fine Laminated Sand)					
5B	75.7	3.78E+06	1.05E+05	<6.40E+03	--
5A	76.4	6.52E+06	1.81E+05	<2.59E+04	--
6B	79.9	3.63E+07	1.64E+06	<4.17E+04	--
6A	80.6	5.31E+07	2.41E+06	<6.29E+04	--
7B	84.1	8.06E+06	2.26E+05	<4.16E+04	--
7A	84.8	2.14E+07	5.97E+05	<5.20E+04	--
7A1	84.6	9.57E+07	4.34E+06	--	--
8B	88.3	5.03E+06	1.41E+05	<9.86E+03	--
8A	89.0	5.55E+05	1.69E+04	<1.22E+03	--
9B	92.5	1.29E+04	1.91E+02	1.23E+01	3.19E+00
9A	93.1	1.71E+02	3.28E+00	2.49E+01	4.40E+00
10B	96.6	6.31E+02	1.00E+01	1.55E+01	1.45E+00
10A	97.3	4.51E+02	7.23E+00	1.82E+01	1.52E+00
11B	101	1.19E+04	1.86E+02	<2.46E+01	--
11A	101.7	9.12E+02	1.46E+01	2.73E+01	3.55E+00
12B	104.9	7.81E+02	1.23E+01	2.20E+01	2.82E+00
12A	105.6	3.37E+02	5.50E+00	2.66E+01	3.58E+00
13B	113.1	5.82E+03	8.95E+01	2.01E+01	3.08E+00
13A	113.8	5.21E+02	8.12E+00	1.64E+01	1.83E+00
14B	121.3	1.16E+03	1.78E+01	1.98E+01	3.37E+00
14A	122.0	8.37E+02	2.40E+01	3.01E+01	2.70E+00
Plio-Pleistocene Subunit (Fine-Grained Mud) [PPlz]					
15B	129.4	5.31E+02	8.65E+00	2.53E+01	5.50E+00
15A	130.1	5.92E+02	9.78E+00	2.47E+01	1.66E+00
16B	137.5	4.62E+03	7.13E+01	2.57E+01	4.11E+00
16A	138.2	9.79E+01	2.09E+00	2.52E+01	1.94E+00
17B	144	7.43E+02	1.17E+01	2.05E+01	5.16E+00
17A	144.6	1.75E+02	3.08E+00	2.58E+01	3.25E+00

Technetium-99 is found at elevated concentrations throughout the SX-108 slant borehole. The technetium-99 elevated concentration pattern (listed as pCi/mL in Table B.17) shows an apparent bimodal distribution in the primary high contamination zone between 26 and 40 m [85 and 130 ft] bgs in the bottom half of subunit H2 and in subunit PPlz (Figure B.23). As with other constituents, the low technetium-99 concentration at 32 m (105.6 ft) bgs creates this distribution. The largest concentration peak occurs at 30 m (97 ft) bgs at a maximum concentration of about 237,000 pCi/mL. This pattern closely mimics the nitrate concentration distribution. It is probable that the bottom of the technetium-99 range was not reached in this sampling effort. Chromium concentration values (listed as mg/L in Table B.17) increase above background beginning at 20 m (68 ft) bgs and show maximum values between 25 and 40 m (81 and 130 ft) bgs. The peak concentrations of greater than 22,000 mg/L occur at 30 m (97 ft) bgs. The deepest entire chromium range may have been captured by these soil samples as indicated by very small concentrations in the two deepest samples. The occurrence of the maximum chromium range slightly higher in the soil column relative to technetium-99 indicates some retarding chemical mechanism has slowed chromium migration relative to technetium-99. Work completed by the S&T activity (Appendix D, Section D.4.1) indicates that iron(II)-rich minerals in the vadose zone soil reduce the oxidation state of a fraction of the chromium in solution from +6 to +3. In the +3 state, chromium is removed from solution by sorption or coprecipitation in iron(II)-rich minerals.

Other constituents that may have been placed into the soil column by the tank SX-108 leak include iodine-129, selenium, and molybdenum. The iodine-129 measurements are difficult to obtain and often suspect, but in this case there does appear to be measurable concentrations between 24 and 40 m (80 and 130 ft) bgs in 4 samples. The maximum concentration of about 43,000 pCi/L occurs at 24 m (80 ft) bgs and values decrease to about 19,000 pCi/L at the bottom of the SX-108 slant borehole, suggesting that the bottom of the iodine-129 contamination zone occurs below the borehole. These concentrations are three orders of magnitude less than technetium-99 concentrations in the same depth interval. Elevated selenium concentrations show a pattern that is nearly identical to technetium-99. Elevated molybdenum concentrations are more restricted and lie between 24 and 28 m (80 and 93 ft) bgs.

B.4.4 CONTAMINANT CONCENTRATIONS

Contaminant concentrations at the SX-108 slant borehole were not analyzed

B.4.5 CHEMICAL INTERACTIONS

No specific experiments were completed on soils from the SX-108 slant borehole to quantify geochemical reactions influencing contaminant migration. Dominant chemical reactions affecting radionuclides and tank fluid chemicals are inferred from the relative location of these constituents in the soil column, comparison of acid-leachable versus water-leachable concentrations for specific contaminants, and general knowledge of the tank fluid chemistry. Greater contaminant mobility is inferred from the occurrence of high concentration zones deeper in the vadose zone and smaller differences in dissolved concentrations leached by water versus acid. Empirical in situ distribution coefficient estimates are summarized in Table B.18.

Sample ID	Vertical Depth (ft bgs)	Dilution Factor	Water:Soil Ratio	Tc-99 (pCi/mL)	U (µg/L)	Cr* (mg/L)	As (µg/L)	Se (µg/L)	Mo (µg/L)	Ag (µg/L)	Cd (µg/L)	Pb (µg/L)
1A	55.1	23.13	1.00	<392	(35.9)	(0.21)	(875)	<1157	305	(2.31)	(30.1)	1253389
1A-Dup	55.1	23.13	1.00	<392	(28.9)	(0.22)	(798)	<1157	347	<57.8	<57.8	4196
3A	67.9	36.88	1.02	(125)	140.14	(29.1)	(1239)	<1844	11446	<92.2	(3.69)	(679)
4A	72.2	36.15	1.00	(61)	209.67	(27.8)	(3687)	<1808	2176	<90.4	<90.4	(95.8)
5A	76.4	21.36	1.00	(217)	(98.3)	75.1	(1772)	(145)	3036	(32.0)	<53.4	(334)
6A	80.6	27.18	1.00	1106	(32.6)	13150	(266)	(1298)	127610	(216)	279	(78.8)
7A	84.8	16.20	1.00	16485	1433.7	5018	(2019)	984.2	90874	(183)	211	(953)
8A	89.0	16.61	1.00	47439	(43.2)	13782	(507)	2477	40238	(276)	105	(74.7)
9A	93.1	42.56	1.00	168400	(46.8)	21817	(1290)	5612	7510	(12.8)	(4.26)	(1221)
10A	97.3	52.34	1.00	237279	(55.0)	20838	(1675)	8615	871	(15.7)	<131	(325)
11A	101.7	31.78	1.00	144287	(6.36)	28.1	(753)	3849	184	<79.5	<79.5	(89.0)
12A	105.6	4.69	1.00	2792	(2.35)	0.98	(23.5)	(37.5)	56.7	<11.7	<11.7	(9.8)
13A	113.8	13.38	1.02	96874	(13.4)	5766	(561)	3182	3180	(8.03)	(14.7)	(33.5)
14A	122.0	8.69	1.04	58820	(5.65)	2588	(422)	1954	258	(5.21)	(0.87)	(45.2)
14A-Dup	122.0	8.38	1.00	64773	(7.12)	2913	(440)	2249	231	(5.03)	<21.0	(21.8)
15A	130.1	5.74	1.00	66072	6.89	1931	(443)	2360	78.6	(3.44)	(0.00)	(12.6)
16A	138.2	13.31	1.00	19255	(18.6)	(0.26)	(82.5)	(419)	181	<33.3	(2.66)	(58.6)
17A	144.6	5.08	1.00	2800	5.08	(0.02)	(20.8)	(69.1)	100	(0.51)	<12.7	(26.9)

Note: Values in parentheses are those that are below limit of quantification.

*Higher chromium values are from ICP-OES, not ICP-MS. Note chromium values are in mg/L

ICP = inductively coupled plasma.

MS = mass spectrometer.

OES = optical emission spectroscopy.

Figure B.23. Trace Metals Calculated and Actual Porewaters
for SX-108 Slant Borehole Sediments

Sample ID	Depth (ft bgs)	Lith. Unit	Distribution Coefficient Values (mL/g)						
			Cesium-137	Technetium-99	Uranium	Chromium	Arsenic	Selenium	Molybdenum
01A	55.1	H1a	230.3	indeterm.	13	423	3.02	indeterm.	1.53
01A-dup	55.1	H1a	--	indeterm.	14	749	8.34	0.11	18.26
03A	67.9	H1	25.7	0.04	5	4.26	1.44	indeterm.	0.16
04A	72.2	H2	72.9	indeterm.	3	4.32	0.64	indeterm.	0.42
05A	76.4	H2	99.3	-0.01	8	2.92	2.68	1.26	0.44
06A	80.6	H2	2.3	0.01	24	0.01	16	0.11	0.06
07A	84.8	H2	4.2	-0.01	0	0.18	2.37	0.21	0.00
08A	89	H2	24.8	-0.02	18	0.05	10	0.06	0.19
09A	93.1	H2	6.5	0.00	14	0.01	3.38	0.02	0.04
10A	97.3	H2	10.2	0.00	12	0.01	2.49	0.02	0.46
11A	101.7	H2	>49.7	0.00	114	1.04	5.74	0.04	3.01
12A	105.6	H2	>120.7	-0.02	588	24.1	461	7.52	4.72
13A	113.8	H2	>46.5	0.00	459	0.04	10	0.06	0.79
14A	122	H2	307.4	0.01	168	0.06	14	0.10	3.21
14A-dup	122	H2	--	-0.01	132	0.03	13	0.12	3.36
15A	130.1	PPIz	>136.7	-0.02	139	0.04	8.32	0.10	7.84
16A	138.2	PPIz	>13.9	0.02	63	84.9	39	0.55	3.02
17A	144.6	PPIz	35.6	0.11	223	1864	303	4.58	15.7

Generally speaking, the data suggest that tank SX-108 fluid chemistry had a substantial, but limited, effect on contamination behavior at the SX-108 slant borehole. Given the depth below the tank SX-108 bottom at which very high concentrations of cesium-137 occur (essentially, the entire thickness of subunit H2), cesium-137 was initially highly mobile in the leaked tank fluid. Various types of sorption experiments completed by the S&T group (Appendix D, Section D.3.0) shows that the very high concentrations of cesium-137, sodium, and to a lesser extent potassium in the tank SX-108 fluid created local conditions where sodium preferentially occupied soil sorption sites in soils and preventing cesium-137 sorption. These conditions were short-lived and confined to subunits H1 and H2 as shown by the current limited distribution of cesium-137. Over time natural infiltration and recharge subsequently separated sodium from cesium-137, permitting cesium-137 to sorb in situ. The current degree of cesium-137 mobility was determined by comparing the amount of cesium-137 removed by water versus total activity measured by gamma. The in situ distribution coefficient for cesium-137 varies from about 2 to 300 mL/g in the sediments in the borehole where distribution coefficient values tend to correspond inversely to the salinity level.

Tank fluids also increased amounts of other constituents in the soil column, but had little effect on the chemical behavior of contaminants other than cesium-137 in the sense that chemical reactions between tank fluid constituents and the soil column environment were largely controlled by soil-soil water reactions. Constituent anions (e.g., nitrate and technetium-99) have migrated the most rapidly and mark the leading edge of vertical tank fluid migration. The technetium-99 in situ distribution coefficient was determined by comparing acid versus water leached concentrations and does not exceed 0.1 mL/g over the whole zone of contamination. Chromium was slightly retarded relative to technetium-99 and nitrate, presumably because of oxidation reduction, allowing fixation on soil. Generally, the in situ distribution coefficient values were very small except for the soil samples between 17 and 23 m (55 and 76 ft) bgs where the distribution coefficient value between about 3 and 430 mL/g was estimated. These numbers suggest that maximum oxidation reduction occurred near the tank bottom.

Other constituent cations have migrated varying distances depending on the strength of retardation mechanisms. Sodium concentrations, being relatively high, successfully completed for sorption sites in vadose zone soils, were somewhat retarded. Calcium, magnesium, and indigenous strontium were displaced by sodium and pushed ahead of sodium during migration.

B.4.6 GROUNDWATER MEASUREMENTS

Groundwater measurements were not taken at the SX-108 slant borehole.

B.5.0 BOREHOLE SEDIMENT ANALYSIS

This section summarizes data reported in *Characterization of Uncontaminated Sediments from the Hanford Reservation – RCRA Borehole Core and Composite Samples* (Seme et al. 2001a) taken from two boreholes (299-W22-48 and 299-W22-50) drilled east of the S and SX tank farms (Figure B.1) as RCRA groundwater monitoring wells. Relative to vadose zone characterization, soil samples taken in the vadose zone represent undisturbed soils that have the soil characteristics found under the S and SX tank farms prior to contamination from tank leaks. The most important data collected from these boreholes include the physical soil properties and the porewater chemistry derived from water extractions, acid extractions, and porewater squeezings.

B.5.1 GEOLOGY

Geology at boreholes 299-W22-48 and 299-W22-50 are described in the following sections.

B.5.1.1 Borehole 299-W22-48

Borehole 299-W22-48 was drilled for the RCRA Groundwater Monitoring Project. Samples were collected via continuous split spoon to a depth of 59 m (193.5 ft) bgs; the sampling effort was sponsored by the S&T activity. Grab samples were taken at 1.5 m (5 ft) intervals. Samples were obtained to support S&T activity research addressing characteristics of noncontaminated sediments.

B.5.1.1.1 Hanford formation. Sediments of the Hanford formation were penetrated from the surface to 41.3 m (135 ft) bgs. Subunits H1 and H2 were present.

- **Subunit H1** – Two distinct coarse-grained intervals (gravelly sand to gravel) were identified within relatively uniform medium-grained sand; an upper zone at 12.5 to 15.3 m (41 to 50 ft) bgs and a lower zone at 17.7 to 18.6 m (58 to 61 ft) bgs. These gravelly intervals have been identified in surrounding vadose zone boreholes and wells based on geophysical log correlations (Sobczyk 2000) but have not been readily identified in the geologic grab samples. The base of subunit H1 is estimated to lie at 18.6 m (61 ft) bgs.
- **Subunit H2** – Subunit H2 extends to 41.3 m (135 ft) bgs, and has been described as a fine to medium-grained sand which becomes finer with depth. Numerous silt laminae are noted in the split-spoon samples collected from this subunit at this location.

B.5.1.1.2 Plio-Pleistocene Unit. The two Plio-Pleistocene subunits include the upper subunit PPlz, characterized by a relatively high silt content, and the lower subunit PPlc, characterized by secondary, pedogenic, calcium-carbonate cement.

- **Subunit PPlz** – Subunit PPlz is recognized on the gamma logs and is present from 41.3 to 44.6 m (135 to 146 ft) bgs. This gamma signature reflects the downward decreasing grain size from silty sand to silt typical of the unit in this area.

- **Subunit PPlc** – Subunit PPlc is present from 44.6 to 45.5 m (146 to 149 ft) bgs at this location. The carbonate-rich unit is at a moderately higher elevation at this location than at sites further south.

B.5.1.1.3 Ringold Formation. Two subunits of the Ringold Formation have been tentatively identified at borehole 299-W22-48, the member of Taylor Flat and the member of Wooded Island. The interpretation of the Ringold Formation in this borehole differs significantly from other nearby wells.

- **Member of Taylor Flat** – At borehole 299-W22-48, a fairly uniform, silty, sandy, gravel unit extending from 45.5 to 58.6 m (149 to 192 ft) bgs has been tentatively identified as the member of Taylor Flat. This unit has not been identified elsewhere in the near vicinity and may actually be representative of the more commonly identified member of Wooded Island unit E.
- **Member of Wooded Island** – Member of Wooded Island unit E silty-sandy gravels have been identified by an increase in moisture at 58.6 m (192 ft) bgs that extends to the water table at 69 m (226 ft) bgs.

B.5.1.2 Borehole 299-W22-50

The vadose zone portion of borehole 299-W22-50 penetrated strata belonging to the Hanford formation, the Plio-Pleistocene unit, and the Ringold Formation. The upper 6.1 m (20 ft) of this borehole were not sampled, drilling in *this* portion of the borehole was done with a cable-tool deployed core barrel, and no intact samples were available for geologic logging.

Field descriptions of that portion of the borehole indicate it penetrated fine sand, coarse sand, and gravel/sand facies.

B.5.1.2.1 Hanford formation. Sediments of the Hanford formation were penetrated from the ground surface to an estimated depth of 39.3 m (129 ft) bgs. Subunits H1 and H2 were present.

- **Subunit H1** – From a depth of 6.1 m (20 ft) bgs to approximately 16.1 m (53 ft) bgs the sediments logged consist of fine sand facies with lesser coarse sand facies. Stratification commonly observed in this interval include planar laminae, normally graded bedding and silty interbeds. Some evidence of planar and trough cross-bedding in the form of low-angle bedding intersections were observed. A few structures suggestive of clay skins on clastic dikes were noted. Minor pebble gravel, occurring as isolated clasts, is found in the lowermost 0.9 m (3 ft) of the interval.

Approximately 2.9 m (9.5 ft) of the gravel/sand facies underlies the sandy strata. The contact between these intervals is relatively sharp. Evidence of poorly developed planar and low angle bedding, suggested by coarse-fine grain size alterations is present. No clast-supported pebble gravel was observed in *this* interval.

- **Subunit H2** – A sandy interval from 19 to 39.3 m (62.5 to 129 ft) bgs is interpreted to be subunit H2. The upper 1.7 m (5.5 ft) consist predominately of well-stratified, friable, coarse sand. This sand appears to be unweathered and displays a mixed mafic/felsic mineralogy similar to the matrix sand in the overlying gravelly interval. The remainder

of this sand interval consists predominantly of planar laminated to ripple cross-laminated fine sand facies. Other observed stratification includes normally graded bedding, planar cross bedding and trough cross bedding. Two paleosols are present in the sandy interval at 22.9 m (75 ft) bgs and 31.4 m (103 ft) bgs. Poorly developed blocky peds, possible burrow traces, organic debris, and increased calcium carbonate content is evident in the uppermost of the two paleosols. The deeper paleosol is less well developed, displaying poorly developed traces of burrowing and mottling.

B.5.1.2.2 Plio-Pleistocene Unit. The two Plio-Pleistocene subunits include the upper subunit PPlz, characterized by a relatively high silt content, and the lower subunit PPlc, characterized by secondary, pedogenic, calcium-carbonate cement.

- **Subunit PPlz**– A fine sand/silt facies becomes dominant at 39.3 m (129 ft) bgs. This facies is consistent with the unit described as subunit PPlz in other boreholes in the vicinity of borehole 299-W22-50. This facies displays an increase in the occurrence of silt and the appearance of intercalated silt facies horizons greater than 0.15 m (0.5 ft) thick. Ripple cross-lamination and planar laminae are well developed in the sandy portions of the interval, which extends to 41.9 m (137.5 ft) bgs.
- **Subunit PPlc** – A well-developed paleosol at 41.9 m (137.5 ft) bgs marks the top of subunit PPlc. This paleosol is 0.15 m (0.5 ft) thick and displays moderately well developed beds, bedding is disrupted to massive, and stage I/II calcium carbonate is present. The remainder of the carbonate-rich interval consists of approximately 1.4 m (4.5 ft) of silt, sand, and gravel divided into: (1) approximately 0.46 m (1.5 ft) of conglomerate with a carbonate overprint; (2) somewhat greater than 0.3 m (1 ft) of silty paleosol; and (3) a basal conglomerate with carbonate overprint. The presence of stage II/III carbonate in the form of clast coatings, discontinuous stringers, and concretions indicates this is the Plio-Pleistocene carbonate rich subunit PPlc.

B.5.1.2.3 Ringold Formation. The top of the Ringold Formation is encountered at 43.4 m (142.5 ft) bgs where calcium carbonate content decreases markedly. The uppermost Ringold Formation strata encountered in this well consist of variably indurated conglomerate about 3.7 m (12 ft) thick that has a mixed basaltic/felsic sand matrix. The more felsic portions of the interval display yellow to yellow-brown color typical of many Ringold Formation deposits. However, the mafic content of these sediments is high enough to give the sand matrix a non-typical salt and pepper appearance.

In the interval 47.1 to 49.7 m (154.5 to 163 ft) bgs, coarse, variably indurated, crudely stratified sand with minor pebbles is present. The mineralogy of this sand is similar to the matrix sand in the overlying conglomerate. From 49.7 to 50.5 m (163 to 165.5 ft) bgs another conglomerate unit is penetrated. From 50.5 to 53.8 m (165.5 to 175 ft) bgs a sandy unit is present. This sandy unit is locally silty and displays abundant evidence of disrupted bedding and a white-gray color in the silty parts. The sand is calcium carbonate poor and the mafic content is greater than 25%.

At 53.5 m (175 ft) bgs conglomerate was again encountered, and at 53.8 ft (176.5 ft) bgs split-spoon sampling was suspended. Based on the abundance of gravel and absence of paleosol

facies in the Ringold Formation in this borehole the entire interval is assigned to the member of Wooded Island unit E.

B.5.2 GEOPHYSICAL AND PHYSICAL PROPERTY MEASUREMENTS

Downhole geophysical and physical measurements (Figures B.24 and B.25) for the RCRA borehole sediments analysis included high-purity germanium spectral gamma logs; laboratory measurements of soil moisture content, neutron-neutron logs from the surface to the unconfined aquifer of both boreholes (249 ft [76 m] and 247 ft [75m] for 299-W22-48 and 299-W22-50, respectively); and soil suction measurements (Figure B. 12). Outstanding geophysical data that distinguish stratigraphic units in the vadose zone include high moisture content and low natural gamma levels in subunit PPlc. Subunit PPlz shows relatively high natural gamma levels and low moisture content. Small silt-rich zones are indicated in subunit H2 by high moisture content. Soil suction measurements generally show drainage in the Hanford formation but not in the Plio-Pleistocene unit and below.

B.5.3 SOIL WATER CHEMISTRY MEASUREMENTS

In addition to soil physical property measurements (Section B.5.2), an extensive water chemistry analysis has been completed for samples collected between the surface and 59 m (192 ft) bgs in borehole 299-W22-48 and between the surface and 53 m (174 ft) bgs for borehole 299-W22-50. The primary means of measuring porewater composition was to add deionized water to soil samples to generate enough water for performing analyses. By back-calculating for the dilution introduced by the added water, 'true' concentrations were derived. For a few samples porewater was directly separated from the same soil sample or one nearby and analyzed directly. By comparing the dilution-corrected water extract data with the porewater data in these few samples, an indication of the closeness of the water extract chemistry to original water chemistry was determined. In general, comparisons were not exact but concentration values were generally within a factor of two or better, agreement improved with increasing constituent concentration, and both sets of data showed similar concentrations versus soil depth correlations. Thus, the water extract method is an effective tool for evaluating tank fluid interactions with vadose zone soil.

Water extract pH and electrical conductivity measurements with depth are listed and graphed in Table B.19 and Figure B.26 for borehole 299-W22-48 and listed in Table B.20 for borehole 299-W22-50. The pH values in both boreholes fall into a normal range (7 to 8.5) except at 18 to 21 m (60 to 68 ft) bgs in borehole 299-W22-50 where elevated pH values (about 10 and 9) are measured. The reason for this increase is not known. Elevations in electrical conductivity values are not observed. A range of 50 to 500 $\mu\text{S}/\text{cm}$ are present in these samples.

Water extract anion concentrations as a function of depth are listed in Table B. 19 for borehole 299-W22-48. Nitrate, chloride, and sulfate concentrations with depth are shown in Figure B.27. Other than enrichment of subunit PPlc in nitrate and sulfate, the profiles are undistinguished. In borehole 299-W22-50, anion data have no distinguishing features other than slight elevations of nitrate and sulfate in subunits PPlz and PPlc.

Figure B.24. Vadose Zone Stratigraphy for Borehole 299-W22-48

Figure B.25. Vadose Zone Stratigraphy for Borehole 299-W22-50

**Table B.19. Borehole 299-W22-48 pH, Electrical Conductivity,
Alkalinity, and Anions in 1:1 Water Extracts (2 Sheets)**

Constituent Sample		pH	EC (μ S/cm)	Alk (mg/L CaCO ₃)	F (mg/L)	Cl (mg/L)	NO ₂ (mg/L)	NO ₃ (mg/L)	PO ₄ (mg/L)	SO ₄ (mg/L)
Depth (ft bgs)	Strat. Unit									
1	H1a				1.56	1.27	<0.1	7.06	0.21	2.42
6	H1a				1.90	0.42	<0.1	7.94	<0.1	5.48
9.5	H1a				1.43	0.39	<0.1	5.89	0.27	8.79
12.5	H1a				3.04	0.32	<0.1	4.37	0.24	5.64
14.5	H1a				2.65	0.30	<0.1	4.46	0.29	14.62
17	H1a				2.66	0.35	<0.1	7.10	0.37	15.20
19.5	H1a				1.74	0.72	<0.1	9.79	<0.1	15.70
22	H1a				1.03	0.49	<0.1	14.50	0.35	16.90
24.5	H1a				0.95	0.37	<0.1	5.27	0.34	18.20
27	H1a				1.39	0.49	<0.1	11.00	0.28	18.30
29.5	H1a	7.38	224	47.94	0.95*	0.32*	<0.1	7.89*	0.27*	20.68*
32	H1a	7.97	171	41.60	0.62	0.26	<0.1	6.97	0.30	9.14
34.3	H1a				0.79	0.39	<0.1	5.20	0.63	9.88
37	H1a				0.72	1.43	<0.1	11.90	0.28	14.80
39.5	H1a	7.39	180	33.14	0.55	0.65	<0.1	13.75	<0.24	14.75
42	H1				0.74	0.43	<0.1	3.99	0.13	11.85
44.5	H1				0.63	0.42	<0.1	3.69	0.18	18.40
47	H1	7.30	126	28.91	0.58**	0.24**	<0.1	2.76**	0.13	9.26**
50	H1				0.65	0.84	<0.1	10.90	0.25	12.10
53.5	H1				0.49	0.53	<0.1	2.46	<0.1	10.10
56	H1	7.20	142	NA	0.45	1.05	<0.1	1.00	0.13	11.47
57.5	H1				0.57	1.72	<0.1	7.07	0.12	13.40
74.5	H2	7.395	216	36.00	0.50	5.06	<0.1	7.28	0.33	24.06
91.5	H2				0.60	4.83	<0.1	8.44	0.39	13.60
101.5	H2				0.63	5.48	<0.1	9.82	0.34	17.15
106.5	H2	7.70	177	33.84	0.33	6.45	<0.1	5.19	<0.1	10.40
115.5	H2	7.39	182	38.07	0.36	2.28	<0.1	7.55	0.38	12.30
136	PP1z	7.20	214	40.19	0.45	1.32	<0.1	22.70	0.50	11.90
143.5	PP1z	7.12	186	34.55	0.27	0.71	<0.1	16.20	0.35	11.10
146	PP1c	7.39	441	47.47	0.91	3.57	<0.1	75.20	0.17	44.40
148.5	PP1c	7.48	291	41.6	1.27	1.84	<0.1	42.80	<0.1	16.90

Table B.19. Borehole 299-W22-48 pH, Electrical Conductivity, Alkalinity, and Anions in 1:1 Water Extracts (2 Sheets)

Constituent Sample		pH	EC (μ S/cm)	Alk (mg/L CaCO ₃)	F (mg/L)	Cl (mg/L)	NO ₂ (mg/L)	NO ₃ (mg/L)	PO ₄ (mg/L)	SO ₄ (mg/L)
Depth (ft bgs)	Strat. Unit									
151	Rtf	7.56	208	49.35	1.21	1.68	<0.1	4.16	<0.1	5.45
163.5	Rtf	7.46	117	29.96	0.49	0.45	<0.1	6.95	0.11	1.69
170	Rtf	7.40	116	31.02	0.46	0.49	<0.1	7.34	0.21	1.84
172.5	Rtf	7.33	190	31.73	0.50	0.40				
187	Rtf	7.58	53	15.51	0.48	0.59	<0.1	9.91	<0.1	1.86
192	Rwi(e)	7.78	120	18.33	1.37	1.55	<0.1	9.10	0.29	10.00

Note: *Data in *italics* type are average of duplicate extracts. **Data in **bold type** are the average of triplicate extracts.

EC = electrical conductivity.

NA = not analyzed.

Figure B.26. Moisture Content (wt%) of Sediment, pH and Dilution-Corrected Electrical Conductivity of Water Extract and Actual Porewater versus Depth and Stratigraphy for Borehole 299-W22-48

**Table B.20. Borehole 299-W22-50 pH, Electrical Conductivity, Alkalinity,
, ! and Anions in 1:1 Water Extracts**

Constituent Sample		pH	EC (μ S/cm)	Alk mg/L CaCO ₃	F (mg/L)	Cl (mg/L)	NO ₂ (mg/L)	NO ₃ (mg/L)	PO ₄ (mg/L)	SO ₄ (mg/L)
Depth (ft bgs)	Strat. Unit									
20	H1a	7.78	188	52.88	0.72	0.45	<0.1	5.89	0.1	8.56
22.5	H1a	7.72	221	26.79	0.74	1.08	<0.1	4.51	<0.1	13.52
25	H1a	7.68	214	31.73	0.72	0.76	<0.1	3.42	0.2	9.78
27.5	H1a	7.60	214	48.65	0.7	1.88	<0.1	0.63	0.1	19.56
30	H1a	7.65	217	39.48	0.63	4.85	<0.1	2.64	0.15	20.5
32.5	H1a	7.67	186	43.01	0.56	1.62	<0.1	2.51	0.33	11.64
35	H1a	7.49	222	50.06	0.68	0.82	<0.1	0.68	0.29	13.85
37.5	H1a	7.84	203	45.12	0.61	0.67	<0.1	0.57	<0.1	12.51
40	H1a	7.03	184	47.24	0.5	0.57	<0.1	0.36	<0.1	11.49
42.5	H1a	7.11	223	54.29	0.58	0.99	<0.1	1.15	0.16	17.54
47.5	H1a	7.40	224	34.55	0.57	0.83	<0.1	0.46	<0.1	16.37
51	H1a	7.90	181	56.40	0.59	0.45	<0.1	3.09	0.1	8.62
52.5	H1a	7.44	181	32.43	0.39	0.85	<0.1	0.72	<0.1	16.15
55	H1	7.32	216	54.99	0.47	1.34	<0.1	0.25	<0.1	19.18
56	H1	7.35	129	25.38	0.28	0.54	<0.1	1.25	0.12	8.37
60	H1	10.33	553	60.63	0.41	9.33	<0.1	1.82	<0.1	35.71
67.5	H2	9.00	276		0.38	4.84	<0.1	5.49	0.21	21.9
76	H2	8.55	223	21.86	0.36	4.4	<0.1	8.85	0.18	29.7
96*	H2	7.44 $\pm$ 0.02	298 $\pm$ 15	35 $\pm$ 5	0.39 $\pm$ 0.06	23.7 $\pm$ 13	<0.1	10.0 $\pm$ 1.0	0.20 $\pm$ 0.06	28.7 $\pm$ 1.0
111	H2	7.45	296	58.52	0.49	11.47	<0.1	25.51	0.15	23.01
115	H2	7.51	309	55.70	0.51	14.41	<0.1	29.8	0.17	16.6
130	PPlz	7.66	231	89.54	0.41	2.01	<0.1	6.32	0.16	9.63
135	PPlz	8.50	226.5	62.04	0.46	2.31	<0.1	20.99	0.2	18.02
141	PPlc	8.12	246	67 $\pm$ 36	0.80 $\pm$ 0.08	3.3 $\pm$ 0.5	<0.1	11 $\pm$ 1.3	<0.1	22 $\pm$ 2.8
150.5	Rtf	7.77	191	6.35	1.1	1.49	<0.1	<0.1	<0.1	8.62
160.5	Rtf	7.74	135	31.02	0.62	0.76	<0.1	<0.1	<0.1	3.13
174	Rtf	7.75	88	18.33	0.99	4.77	<0.1	10.9	0.13	2.51

*Data are average of duplicate extracts.

EC = electrical conductivity.

Figure B.27. Dilution-Corrected Anion Content of Water Extracts and Anion Concentration in Actual Porewater versus Depth and Stratigraphy for Borehole 299-W22-48

Water extract cation concentrations as a function of depth are listed in Table B.21 and graphed in Figure B.28 for borehole 299-W22-48. Table B.22 provides cation concentrations for borehole 299-W22-50. In both boreholes slight elevations of calcium and natural strontium occur in subunit PPlc because of the relatively high quantities of calcium carbonate. A calcium enrichment anomaly occurs at 60 ft (18 m) bgs in borehole 299-W22-50, which is unexplained.

Trace metal concentrations are shown in Tables B.23 and B.24 for boreholes 299-W22-48 and 299-W22-50, respectively. Slight molybdenum enrichment is seen in subunit PPlc at both boreholes. Also, in borehole 299-W22-48 slight enrichment of selenium occurs in subunit PPlc.

B.5.4 CONTAMINANT CONCENTRATIONS

Contaminant concentrations were not analyzed in the RCRA borehole sediments analysis.

B.5.5 CHEMICAL INTERACTIONS

Chemical interactions were not analyzed in the RCRA borehole sediments analysis.

B.5.6 GROUNDWATER MEASUREMENTS

Groundwater contaminants are present in boreholes 299-W22-48 and 299-W-22-50.

The contaminants are apparently derived both from large regional contaminant plumes (whose sources are a variety of crib, ditch, and trench discharges) and from tank waste. Available contaminant data are listed in Appendix C, Table C.16. Small concentrations of technetium-99, chromium, nitrate, and carbon tetrachloride are present in borehole 299-W22-48. The carbon tetrachloride is ubiquitous in this region. Technetium-99 appears to be increasing and may be derived from S tank farm contamination. The carbon tetrachloride and the nitrate that occur 75 to 80 m (246 to 263 ft) bgs in well 299-W22-50 are assumed to be derived from regional sources. The technetium-99 and nitrate occurring near the top of the aquifer may be derived from the tank SX-115 leak as indicated by the elevated technetium-99/nitrate ratio of 0.1 pCi/μg the same ratio found at well 299-W23-19 (Figure C.25). A more extensive discussion of these and other data postulated as relevant to tank SX-115 leak is provided in Section 3.4.2 of the main text.

Table B.21. Major Cations in 1:1 Water Extracts of Borehole 299-W22-48 Sediment Samples

Stat Unit (ft bgs)	Na (mg/L)	Mg (mg/L)	Al (µg/L)	Si (mg/L)	P (µg/L)	S (mg/L)	K (mg/L)	Ca (mg/L)	Mn (µg/L)	Fe (µg/L)	Sr (µg/L)	Ba (µg/L)
29.5-H1a	28.97	1.42	(35)	17.71	(91)	7.18	4.67	6.78	(1)	49.2	29.7	27.6
32.0-H1a	21.10	1.16	(49)	16.46	(113)	2.95	4.12	6.00	(1)	68.8	21.1	12.2
39.5-H1a	20.09	1.24	(29)	10.57	<500	4.54	3.83	6.66	(1)	(17)	24.3	15.5
47.0-H1	12.70	1.07	(48)	10.46	(2)	3.26	2.93	5.28	(1)	42.5	25.4	21.2
56.0-H1	15.36	2.29	50.7	9.06	(135)	4.00	4.70	8.89	(3)	43.1	37.4	(5)
74.5-H2	16.45	3.56	76.1	9.55	(83)	8.98	4.36	10.75	(1)	45.0	62.0	17.3
91.5-H2	19.14	2.86	286	12.80	(197)	5.30	3.47	9.55	(2)	93.2	49.9	17.0
101.5-H2	20.19	2.75	272	13.64	(169)	6.36	3.45	11.95	(3)	90.9	59.3	29.9
106.5-H2	14.21	2.15	85.0	8.94	(36)	4.14	3.60	9.65	(1)	63.2	48.5	16.9
115.5-H2	14.81	2.27	54.8	11.33	(21)	4.94	3.36	10.47	(1)	58.7	57.1	27.9
136.0-PPlz	16.50	3.21	68.5	11.76	(110)	4.78	3.84	12.92	(1)	39.2	65.9	32.3
143.5-PPlz	11.32	3.66	(10)	8.83	(88)	4.21	3.27	11.23	(1)	(8)	61.0	29.5
146.0-PPlc	22.44	12.21	(5)	26.28	(207)	15.83	5.00	29.60	(0)	(5)	186	29.6
148.5-PPlc	15.29	7.52	(8)	28.10	<500	6.40	3.99	18.47	(0)	95.5	121	24.9
151.0-Rtf	17.55	4.70	(29)	18.91	(81)	2.39	6.11	10.39	(4)	(19)	60.9	16.5
163.5-Rtf	7.24	2.68	(25)	11.73	<500	0.83	2.47	6.65	(0)	(16)	38.2	11.9
170.0-Rtf	7.13	2.93	(31)	12.78	<500	0.89	2.82	7.30	(2)	33.2	41.3	44.6
172.5-Rtf	8.22	2.80	(29)	13.06	(18)	0.70	3.62	7.01	(1)	(21)	39.3	19.0
187.0-Rtf	4.74	0.51	(28)	12.70	(145)	0.77	1.58	1.31	(2)	46.3	(7)	(8)
192.0-Rwi(e)	13.95	0.74	65.2	11.65	(125)	3.84	4.22	1.75	(2)	40.7	(10)	16.5

Note: Values in parenthesis are just below level of quantification but spectra looked good; thus, a tentative value was attributed to data. Data in bold are average of duplicate extracts.

Figure B.28. Dilution-Corrected Cation Content of Water Extracts and Cation Concentrations in Actual Porewater versus Depth for Borehole 299-W22-48

Table B.22. Major Cations in 1:1 Water Extracts for Borehole 299-W22-50

Depth (ftbgs)	Strat. Unit	Na mg/L	Mg mg/L	Al µg/L	Si mg/L	P µg/L	S mg/L	K mg/L	Ca mg/L	Mn µg/L	Fe µg/L	Sr µg/L	Ba µg/L
20	H1a	19.63	1.65	(29)	16.34	(33)	3.11	5.40	7.14	(0)	33.9	31.6	16.9
22.5	H1a	24.74	2.08	(45)	16.61	<500	4.76	6.48	9.49	(1)	96.2	40.2	20.0
25	H1a	20.05	1.40	(30)	14.22	(91)	3.51	5.41	6.32	(0)	30.6	27.5	18.5
27.5	H1a	22.40	2.35	(38)	15.60	(42)	7.10	6.69	10.72	(2)	76.7	48.1	28.8
30	H1a	20.15	2.42	(20)	17.47	(59)	7.18	5.98	11.24	(0)	45.6	52.1	19.9
32.5	H1a	19.79	1.67	(23)	15.40	(91)	4.48	4.86	7.95	(0)	26.3	34.6	18.2
35	H1a	25.40	2.15	(30)	16.63	(54)	5.56	6.82	10.91	(1)	31.7	49.0	26.3
37.5	H1a	22.52	1.97	(21)	16.02	(80)	5.08	6.37	9.98	(0)	33.2	44.7	19.8
42.5	H1a	122.12	2.62	(25)	17.63	<500	6.85	7.09	12.86	(0)	(22)	55.9	17.5
45	H1a	21.62	2.52	(30)	18.01	(50)	7.06	7.19	12.28	(0)	(22)	55.5	21.3
47.5	H1a	22.33	2.63	(25)	17.90	(41)	6.47	7.31	13.13	(0)	(23)	59.9	21.1
51	H1a	17.25	1.84	(22)	17.61	(126)	3.39	5.20	9.15	(0)	35.2	39.9	13.7
52.5	H1a	15.17	2.17	(34)	13.94	(52)	6.26	5.57	10.12	(0)	(19)	46.3	20.3
55	H1	19.45	2.79	(36)	15.40	(56)	7.31	6.56	12.72	(1)	33.7	58.3	27.5
56	H1	11.06	1.77	(47)	9.01	(76)	3.20	4.09	5.74	(1)	(21)	26.8	14.6
60	H1	28.12	0.03	379	28.04	(145)	13.61	10.05	51.55	<10	(7)	176	44.9
67.5	H2	16.36	3.03	103	10.67	(154)	8.21	4.69	12.62	(1)	109	56.8	15.3
76	H2	16.34	2.79	75.1	10.51	(81)	10.64	4.01	14.10	(0)	59.7	58.7	16.4
96	H2	23.18	4.29	(27)	9.95	(139)	11.20	5.93	19.17	(0)	(18)	85.6	26.7
111	H2	22.41	3.93	(14)	11.51	(67)	9.01	5.66	17.85	(0)	(11)	79.7	30.1
115	H2	24.33	4.15	(26)	10.23	(51)	6.75	5.49	18.50	(3)	33.1	85.4	35.5
116	H2	17.48	2.14	308	14.43	(257)	4.05	2.66	10.45	(2)	98.6	46.1	25.8
130	PPlz	18.37	4.03	(29)	9.96	(78)	4.13	3.78	16.15	(2)	(19)	71.8	28.6
135	PPlz	20.96	4.61	(13)	10.58	(179)	7.07	4.72	15.73	(0)	(12)	70.3	28.7
140	PPlc	17.01	3.51	277	14.99	(131)	6.16	3.04	11.41	(3)	117	57.4	34.0
141	PPlc	20.13	5.28	(20)	21.56	(33)	8.93	4.71	17.09	(0)	(13)	82.9	22.7
150.5	Rtf	17.33	3.31	370	13.81	(129)	3.87	4.63	10.44	15.2	352	59.6	15.3
160.5	Rtf	10.02	2.33	(38)	13.98	(88)	1.52	3.60	8.41	(2)	(24)	40.5	16.8
174	Rtf	6.69	0.90	106	13.81	(123)	1.13	2.20	2.98	(2)	44.7	(14)	(5)

Table B.23. Trace Metals in 1:1 Water Extracts of Borehole 299-W22-48 Sediments

Units (ft bgs)	B (µg/L)	Cr*	Co	Ni	Cu	Zn	As*	Se*	Mo*	Tc*	Pb*	U*
	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)	(µg/L)
29.5-H1a	(8)	(0.32)	<10	<100	<25	30.9	37.5	(0.69)	3.97	(0.00)	(0.16)	2.84
32.0-H1a	(3)	(0.37)	1.4	<100	<25	15.0	32.1	(0.15)	2.35	(0.00)	(0.03)	1.47
39.5-H1a	(0)	(0.39)	<10	<100	<25	22.7	21.6	(1.06)	4.81	(0.00)	(0.29)	1.76
47.0-H1	<100	(0.19)	1.1	<100	<25	22.3	9.45	(0.29)	1.20	(0.00)	(0.25)	0.530
56.0-H1	(4)	(0.07)	1.0	<100	<25	16.3	9.52	(0.23)	11.35	(0.00)	(0.16)	1.47
74.5-H2	(6)	0.470	<10	<100	<25	23.1	21.6	(0.65)	7.08	(0.00)	(0.18)	0.430
91.5-H2	2003	0.551	1.3	<100	<25	15.7	22.5	(3.84)	17.64	(0.00)		0.455
101.5-H2	1996	0.985	<10	<100	<25	20.0	19.2	5.77	24.2	<0.025		0.430
106.5-H2	(6)	0.530	<10	<100	<25	24.5	17.1	(2.25)	12.1	(0.00)	(0.22)	0.375
115.5-H2	(10)	0.940	1.8	<100	(0)	26.9	21.2	(3.15)	10.6	(0.00)	(0.31)	0.530
136.0-PPlz	(8)	0.665	1.5	<100	<25	44.1	26.4	12.9	9.5	(0.00)	(0.14)	0.510
143.5-PPlz	(7)	(0.21)	1.1	<100	<25	25.6	9.20	6.55	17.3	<0.025	(0.14)	0.970
146.0-PPlc	(11)	1.86	1.4	<100	<25	29.3	8.44	36.50	57.2	(0.00)	(0.08)	7.90
148.5-PPlc	(3)	0.690	<10	<100	<25	23.3	10.8	14.8	9.9	(0.00)	(0.75)	5.68
151.0-Rtf	(4)	(0.07)	0.9	<100	(2)	22.1	8.56	(3.22)	7.58	(0.00)	(0.04)	2.48
163.5-Rtf	<100	(0.05)	2.0	<100	<25	27.8	15.0	(2.67)	5.17	(0.00)	(0.01)	0.245
170.0-Rtf	(0)	(0.24)	0.0	<100	<25	86.8	12.4	(3.39)	5.99	<0.025	(0.22)	0.565
172.5-Rtf	(1)	(0.17)	2.2	<100	<25	23.8	10.6	(1.80)	6.94	(0.00)	(0.06)	0.920
187.0-Rtf	<100	(0.19)	1.4	<100	<25	26.3	6.31	4.25	3.54	(0.00)	(0.09)	0.000
192.0-Rwi(e)	(9)	(0.26)	0.8	<100	<25	96.7	6.80	5.78	7.14	<0.025	(0.13)	0.032

Note: Values in parenthesis are just below level of quantification but spectra looked good; thus, a tentative value was attributed to data. Data in **bold** are average of duplicate extractions.

*ICP-MS instrument was used.

Table B.24. Trace Metals in 1:1 Water Extracts of Samples for Borehole 299-W22-50

Depth (ft bgs)	Strat. Unit	B (µg/L)	Cr* (µg/L)	Co (µg/L)	Ni (µg/L)	Cu (µg/L)	Zn (µg/L)	As* (µg/L)	Se* (µg/L)	Mo* (µg/L)	Tc* (µg/L)	Pb* (µg/L)	U* (µg/L)
20	H1a	(8)	0.910	<10	(6)	(1)	30.3	39.3	<5	1.89	(0.00)	(0.35)	1.11
22.5	H1a	(6)	(0.31)	0.5	(6)	(2)	41.4	34.4	<5	4.81	(0.00)	(0.28)	1.73
25	H1a	(4)	(0.28)	<10	(4)	(1)	48.8	41.3	(0.02)	3.52	(0.00)	(0.84)	1.55
27.5	H1a	(3)	(0.47)	0.1	(2)	(1)	33.6	34.0	(0.14)	6.57	(0.00)	(0.13)	1.44
30	H1a	(5)	(0.32)	<10	(3)	(2)	31.5	13.5	(0.27)	1.62	(0.00)	(0.09)	0.805
32.5	H1a	(3)	(0.41)	0.4	(3)	(1)	30.8	27.0	(0.24)	2.12	(0.00)	(0.01)	1.61
35	H1a	(2)	0.510	0.0	(2)	(1)	31.3	24.3	(0.28)	9.68	(0.00)	(0.03)	2.08
37.5	H1a	(3)	0.625	<10	(2)	(3)	28.6	22.8	(0.21)	12.8	(0.00)	(0.25)	1.72
40	H1a	(4)	0.535	<10	(3)	(1)	42.4	10.1	(0.07)	4.32	(0.00)	(0.02)	1.07
42.5	H1a	(6)	0.590	<10	(4)	(1)	46.7	11.5	(0.17)	6.74	(0.00)	(0.00)	1.15
45	H1a	(5)	(0.49)	<10	(2)	(3)	35.2	13.2	(0.58)	6.05	(0.00)	(0.22)	1.15
47.5	H1a	(5)	(0.49)	<10	(3)	(1)	29.8	11.2	(0.13)	12.54	<0.02	(0.08)	1.21
51	H1a	(0)	(0.39)	<10	(3)	(0)	26.7	12.4	(0.18)	1.03	(0.00)	(0.00)	0.710
52.5	H1a	(2)	(0.32)	<10	(3)	<25	34.8	9.60	(0.50)	3.35	(0.00)	(0.25)	0.565
55	H1	(4)	(0.48)	<10	(4)	(2)	26.9	7.09	(0.31)	14.9	(0.00)	(0.02)	0.820
56	H1	<100	(0.15)	<10	(2)	<25	33.3	9.16	(0.42)	2.81	(0.00)	(0.02)	0.565
60	H1	(11)	48.8	<10	(2)	(3)	33.5	2.95	(0.66)	10.21	(0.00)	(0.02)	0.000
67.5	H2	(3)	0.715	<10	(4)	(2)	34.3	16.6	(0.66)	9.96	(0.00)	(0.21)	0.885
76	H2	(4)	0.760	<10	(4)	(0)	31.4	14.7	(1.14)	4.77	(0.00)	(0.14)	0.565
96	H2	(11)	0.775	<10	(2)	<25	30.2	12.7	(1.22)	14.5	(0.00)	(0.10)	0.567
111	H2	(12)	1.85	<10	(8)	(5)	27.7	13.8	(1.64)	20.2	(0.00)	(0.00)	0.615
115	H2	(14)	0.500	0.0	(6)	(4)	28.7	11.7	(3.40)	17.6	(0.00)	(0.05)	0.810
116	H2	2161	0.705	0.1	(3)	(4)	19.9	29.7	(1.43)	11.1	(0.00)		0.348
130	PPlz	(9)	(0.39)	<10	(3)	(4)	25.5	9.81	(3.12)	15.1	(0.00)	(0.02)	0.935
135	PPlz	(12)	1.65	<10	(5)	(3)	33.3	6.76	5.38	28.1	(0.00)	(0.07)	0.870
140	PPlc	2089	0.925	1.2	<100	(1)	21.1	9.51	(2.00)	25.7	(0.00)		0.975
141	PPlc	(8)	0.725	<10	(4)	(3)	34.9	18.1	(3.14)	63.6	(0.00)	(0.17)	10.24
150.5	Rtf	(5)	0.565	<10	(5)	(3)	31.4	3.61	(0.10)	8.23	(0.00)	(0.10)	0.775
160.5	Rtf	(5)	(0.29)	0.0	(6)	(4)	30.8	3.82	(0.95)	5.96	(0.00)	(0.04)	0.438
174	Rtf	(1)	0.610	<10	(5)	(5)	32.0	3.44	(3.41)	1.61	(0.00)	(0.24)	0.005

Note: Values in parenthesis are just below level of quantification but spectra looked good; thus, a tentative value was attributed to data. Data in bold are average of duplicate extractions.

*ICP-MS instrument was used.

B.6.0 S TANK FARM SHALLOW SOILS INVESTIGATION

A shallow soils investigation (Bratton et al. 2001a) was conducted in the S tank farm to address the source and extent of contamination associated with tank S-104, as well as other nearby locations that could have contributed to the identified vadose zone contamination. Cesium-137 had been reported in the vicinity of this tank (GJPO 1998) through the baseline spectral gamma logging program. Cesium-137 was noted at concentrations greater than the resolution capability of the 35% high-purity germanium tool used. Research into the history of 241-S-104 operations revealed that the tank was subjected to an overfill in 1965. After thorough review of the tanks' construction, a hypothesis was developed that proposed that when the tank was overfilled, the resulting moderate overpressurization caused tank wastes to exit the tank through one or more spare inlet ports. The location of the well shown by the spectral gamma logging to be contaminated is in close proximity to a bank of spare inlet ports at the four o'clock position on the tank. This hypothesis could be tested by collecting gamma distribution data near the tank wall at this position.

A gamma tool deployed via a cone penetrometer was selected as the preferred method of collecting data. The cone penetrometer can be rapidly pushed to the depth of the tank farm excavation, gross gamma data collected as the cone is advanced and spectral gamma analysis could be run to determine those contaminants contributing to the gross gamma signature. Gamma spectra were obtained during this deployment, but are not reported due to the limited window of concentration that can be defined (Bratton et al. 2001b). Finally, it would be feasible to attempt collecting samples should threshold sampling criteria be met.

Eight locations (Figure B.29) were selected to be characterized. These locations were screened for underground utilities using ground-penetrating radar. These ground-penetrating radar screens revealed that the primary site was in close proximity to a shallow electrical service. This site was hand excavated to reveal the true location of the electrical service and then an elongate area demarked through which the cone penetrometer was deployed.

B.6.1 GEOLOGY

The investigation only went through the backfill material. See Appendix C, Section C.4.0 for a description of the backfill.

B.6.2 GEOPHYSICAL AND PHYSICAL PROPERTY MEASUREMENTS

Three locations (CP-04-03, CP-04-04, and CP-04-05) showed gross gamma signatures (Bratton et al. 2001a). Two of these locations (CP-04-04 and CP-04-05) show a bimodal distribution of gross gamma counts (Figures B.30 and B.31). The lowermost zone of high counts, present at all three locations, resides at the base of the tank farm excavation from 12.2 to 13.7 m (40 to 45 ft) bgs. Count rates in this zone ranged from 60,000 to 125,000 counts per second resulting in an instrument dead time exceeding 90%. The upper zone resides between 8.8 and 9.8 m (28.75 and 32 ft) bgs, well above and separated from the base of the excavation. The highest count rates in these two zones were 15,000 and 80,000 counts per second.

Figure B.29. Cone Penetrometer Test Locations in the S Tank Farm

Figure B.30. Distribution of Gross Gamma Concentrations at Location CP-04-04 Down to 50 ft (16 m) Below Ground Surface

Figure B.31. Distribution of Gross Gamma Concentrations at Location CP-04-05 Down to 50 ft (16 m) Below Ground Surface

Samples were collected from immediately below the upper zones of contamination and submitted for laboratory analysis. Because the spectral gamma mode analysis of these portions of the holes did not show a characteristic peak for cesium, the possibility of strontium-90 based Bremsstrahlung-induced peaks were hypothesized. Laboratory analysis of recovered samples showed no contamination. No samples were collected from the highly contaminated lower zones to preclude contamination of people and equipment during recovery.

B.6.2.1 Interpretation of Results Measurements

Each of the cone penetrations was extended to refusal. The majority of the pushes were within the S tank farm excavation. Pushes CP-00-02, -02A and -02B were outside the farm excavation as evidenced by the limited depth to refusal (Table B.25). The base of the farm in all areas investigated is a compacted surface, likely due to extended vehicular compaction during the construction process. (Construction specifications HW-3937, indicate that the zone under the tanks was likely not mechanically compacted prior to placement of the tank bases.)

The compacted portions of the tank farm excavation provide a surface upon which tank derived fluids would spread. Evidence supporting this interpretation is the high count rate materials found in CP-03, -04 and -05 locations in the range of 12.2 to 13.7 m (40 to 45 ft) bgs. The full volume of impacted sediments could not be determined due to the limited depth that could be interrogated. It is probable that contamination resulting from an overfill would also extend beneath the tank.

Two push locations, CP-04 and CP-05, where a high gamma signature was found above the base of the excavation at 9.2 and 9.1 m (30.25 and 29.75 ft) bgs, respectively, support the hypothesis that this S tank farm contamination is due to an overfill of tank S-104. Limitations on how close to a tank wall a mechanized excavation can be performed severely impact full resolution of this leak hypothesis. Figure B.32 is a conceptualization of the extent of contamination associated with tank S-104.

B.6.2.2 Estimate of Inventory Based on Measurements

It was necessary to make a number of assumptions to estimate the possible inventory held in the vadose zone beneath tank S-104. The following outline those assumptions.

- **Extent of contamination** – The contaminants are symmetrically dispersed about the hypothesized source in a circle that is an approximately 12 m (39 ft) radius.
- **Depth of contamination** – Total thickness is 0.3 m (1 ft) based on the depth of greater than 10^6 pCi/g cesium concentration that is cited in G P O (2000).
- **Concentration** – The maximum concentration reported for borehole 40-04-05 (GJPO 2000), which is 2.0×10^6 pCi/g
- **Soil Density** – Throughout subject area is assumed to be 1.8 g/cc.

Table B.25. Summary of Data from Gamma Cone Penetrometers in the S Tank Farm

Location/ Well #	Final Depth (ft)	Cone Datafile	Spectrum Datafile	Spectrum Depth (ft)	Counts/ sec	Sample Depth
CP-00-02 C3049	33.01	527J0001C.DAT				
CP-00-02A C3050	8.10	528J0002C.DAT	28JANB.CHN 28JANC.CHN 28JAND.CHN 28JANE.CHN 28JANF.CHN	1.05 2.05 3.85 5.35 6.85	60 60 45 45 45	
CP-00-02B C3051	15.00	528J0003C.DAT	28JANI.CHN 28JANJ.CHN 28JANK.CHN 28JANL.CHN 28JANM.CHN	1.13 2.55 4.05 5.55 6.75	45 45 45 45 45	
CP-04-03 C3052	46.35	531J0001C.DAT	31JANB.CHN 31JANC.CHN 31JAND.CHN 31JAN3.CHN	43.25 43.65 44.05 45.15	500 2,000 12,000 180,000	
CP-04-04 C3053	44.40	501F0001C.DAT	01FEBB.CHN 01FEBC.CHN 01FEBD.CHN 01FEBE.CHN 01FEBF.CHN 01FEBG.CHN	27.25 28.75 30.25 31.75 38.75 40.25	300 8,700 15,000 2,200 320 60,000	31.75-33.75 28.75-30.70
CP-04-02 C3055	47.02	502F0003C.DAT				
CP-04-11 C3056	50.74	503F0001C.DAT				
CP-04-05 C3057	43.95	503F0004C.DAT	03FEBD.CHN 03FEBE.CHN 03FEBF.CHN 03FEBG.CHN 03FEBH.CHN 03FEBI.CHN 03FEBJ.CHN 03FEBK.CHN	27.05 28.25 29.75 31.25 32.75 34.25 39.25 40.75	450 9,000 80,000 35,000 3,500 300 350 125,000	31.25-33.75
CP-02-05 C3059	39.5	507F0003C.DAT				
CP-02-02 C3060	42.9	508F0001C.DAT				

Based on this gross calculation, approximately 500 curies of cesium-137 would be included in the plume. The total inventory of cesium-137 calculated by MACTEC-ERS (GJPO 2000) is about 10 curies. Neither of these inventory estimates supports the reported 91,000 L (24,000 gal) leak (Hanlon 2001). Based on Jones et al. (2000) the cesium-137 inventory that would result from the reported 91,000 L (24,000 gal) loss would be approximately 1.14×10^4 Ci.

B.6.3 SOIL WATER CHEMISTRY MEASUREMENTS

Soil water chemistry measurements were not taken during the S tank farm shallow soils investigation.

B.6.4 CHEMICAL INTERACTIONS

Chemical interactions were not analyzed during the S tank farm shallow soils investigation.

B.6.5 GROUNDWATER MEASUREMENTS

Groundwater measurements were not applicable to the S tank farm shallow soils investigation.

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APPENDIX C

**NON-WORK PLAN SPECIFIC WORK
AND ASSOCIATED RESULTS**

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LIST OF TERMS

bgs	below ground surface
ESP	Environmental Simulation Program
HDW	Hanford defined waste (model)
HGL	HydroGeologic, Inc.
HLW	high-level waste
MSU	Montana State University
RCRA	<i>Resource Conservation and Recovery Act of 1976</i>
REDOX	reduction-oxidation
SST	single-shell tank
WMA	waste management area

C.1.0 INTRODUCTION

The work plan addenda associated with waste management area (WMA) S-SX were developed for the primary purpose of directing field work (Myers 1997; Henderson 1999; Rogers and Knepp 2000). During the course of conducting the identified field work, other activities were identified that would either complement or supplement that field work. Some 'projects-of-opportunity' that fit within the general scope of the Tank Farm Vadose Zone Project were undertaken. Included in this category were sampling and geological mapping associated with *Resource Conservation and Recovery Act of 1976 (RCRA)* groundwater monitoring wells that were drilled to enhance or maintain the WMA S-SX groundwater monitoring program. Included are the data derived from the monitoring of well 299-W23-19 that was drilled to characterize the vadose zone but converted to a groundwater monitoring well due to the technetium-99 activity of the single sample identified in the work plan (Henderson 1999). Efforts to fully document the history of S and SX tank farm activities continued even though the majority of the information had been garnered for the subsurface conditions description report (Johnson et al. 1999).

As noted in Jones et al. (1998), determination of the contaminant inventory that was lost to the vadose zone is the most pressing need. This inventory was estimated using historical data and then revised based on the data gathered during the drilling of the characterization boreholes called out in the work plan addenda.

An effort to characterize the distribution of moisture in the southern portion of the SX tank farm was undertaken in an attempt to determine if pressurized water lines in that portion of the farm were a possible source of recharge. Those measurements added to the drive to cut-off unnecessary pressurized water lines leading to the tank farm. These measurements also added to the database used by the Science and Technology Program modeling effort reported in Appendix D.

Geochemical characterization of sediments collected from cores during construction of the RCRA groundwater monitoring wells provide a basis against which to judge the impact of tank waste lost to the environment.

Finally, data and analysis of the groundwater provide additional insight into the overall conceptual model of contaminant flow and transport through the vadose zone and into the unconfined aquifer.

C.20 TANK FARM HISTORY

Operating history of the S and SX tank farms was compiled and documented in Johnson et al. (1999). As work proceeded in conjunction with the various work plan addenda, that history was correlated with the new field data and the interpretations of that data. No additional incidents in the history of actual tank farm operations were identified.

Adjacent facilities and operations have been scrutinized in an attempt to further define the potential impact; some potentially important historic records could not be located. The most important of those records concern the inventory of technetium-99 disposed to the 216-S-25 trench during the U-1, U-2 pump-and-treat era. This pump-and-treat system used ion exchange columns to remove uranium from groundwater. The resins were used until uranium breakthrough occurred; this mode of operation ensured that technetium-99 was returned to the environment through the trench. The Hanford Environmental Information System was interrogated to ascertain the levels of technetium-99 in wells surrounding the 200-UP-1 and 200-UP-2 pump and treat operation. The values contained in Hanford Environmental Information System show technetium-99 to have been in the range of 3,000 to 4,000 pCi/L maximum.

C.3.0 LEAK INVENTORY ESTIMATES

The development of credible inventory estimates of chemicals and radionuclides lost to the WMA S-SX vadose zone represents a major component of the characterization activities. This inventory estimate provides both quantitative data for transport modeling and constrains the range of components that need be considered in the risk evaluation. The development of these estimates was based on an extensive review of historical records, previously developed methods for estimating tank waste compositions, extensive field investigation data, and statistical modeling of certain data sets. Highlights of these activities are discussed in Section 3.0 of the main text of this report. More extensive data tables are included in this section.

C.3.1 WASTE COMPOSITION ESTIMATES

There has long been an interest in using flowsheet data from various Hanford Site chemical processes coupled with waste transfer records to develop tank waste inventory estimates (Jungfleish 1984). Researchers at Los Alamos National Laboratory, supported by many individuals associated with the Hanford tank waste characterization program (Agnew 1997) brought the approach developed by Jungfleish to fruition. The Los Alamos National Laboratory task involved two major activities.

- The extensive waste transfer records were centralized into a single document, *Waste Status and Transfer Record Summary (WSTRS Rev. 4)* (Agnew et al. 1997).
- Flowsheet information was coupled with an understanding of the chemistry of each waste stream to develop estimates of solid and liquid compositions for each waste stream.

The composition of each major waste stream was coupled with the waste volumes for each of the transfers into and out of each Hanford Site waste tank. Using simple waste mixing rules for the sum of waste transfers through individual tanks, current waste compositions and total inventories were calculated for each Hanford Site waste tank. This approach is termed the Hanford defined waste (HDW) model (Agnew 1997). The HDW model develops two waste composition estimates:

- Sludge composition, estimated by the tank layering model
- Supernatant composition, estimated by the supernatant mixing model.

The waste composition estimates from the supernatant mixing model module are a combination of liquid and salt cake (Agnew 1997).

Although the driver for the HDW model was to develop 'current' tank inventory estimates, the HDW model provides the capability for developing inventory estimates at any point in time in each tank. As noted above, the HDW model results for selected SX tank farm high-heat tanks are used in Agnew and Corbin (1998) to develop the 'Hanford leak model,' which projects preliminary leak volume estimates for tanks SX-108, SX-109, SX-111, and SX-112. The Agnew and Corbin (1998) approach for developing tank composition estimates at specific points in time was used in estimating tank leak events in WMA S-SX (Jones et al. 2000a). Tables C.1 and C.2 list the waste composition estimates at the times tanks were suspected to have leaked for 10 tanks in the S and SX tank farms (for more details in the development of these tables see discussion in Jones et al. 2000a).

Table C.1. Summary of Chemical Tank Supernate/Salt Concentrations at Time of Leak (2 Sheets)

Tank	S-104	SX-107	SX-108	SX-109	SX-110	SX-111	SX-112	SX-113	SX-114	SX-115
Assumed Leak Date	1965 (mol/L)	Ave. 64-67 (mol/L)	Ave. 65-66 (mol/L)	Ave. 64-67 (mol/L)	1974 (mol/L)	1973 (mol/L)	1969 (mol/L)	1962 (mol/L)	1972 (mol/L)	1964 (mol/L)
Chemicals										
Na	8.671E+00	1.873E+01	1.960E+01	1.519E+01	6.068E+00	5.310E+00	1.319E+01	7.982E+00	8.852E+00	3.593E+00
Al	1.556E+00	3.273E+00	3.361E+00	2.560E+00	7.336E-01	5.270E-01	2.167E+00	1.267E+00	9.692E-01	8.258E-01
Total Fe	3.543E-03	6.878E-03	7.209E-03	5.598E-03	4.216E-03	5.323E-03	3.542E-03	2.967E-03	7.436E-03	2.111E-03
Cr	1.647E-01	3.919E-01	4.128E-01	3.211E-01	6.793E-02	5.862E-02	2.065E-01	1.712E-01	1.015E-01	5.088E-02
Bi	8.951E-09	0.000E+00	0.000E+00	0.000E+00	1.139E-04	1.179E-04	6.395E-06	0.000E+00	1.475E-04	6.627E-08
La	2.205E-14	0.000E+00	0.000E+00	0.000E+00	8.532E-10	1.326E-09	1.575E-11	0.000E+00	1.720E-09	1.632E-13
Hg	3.541E-06	1.154E-07	1.966E-09	0.000E+00	1.518E-06	1.586E-06	1.006E-06	0.000E+00	1.864E-06	6.293E-06
Zr (as ZrO(OH)2)	8.935E-10	0.000E+00	0.000E+00	0.000E+00	1.953E-05	1.614E-05	6.383E-07	0.000E+00	1.959E-05	6.615E-09
Pb	5.666E-04	1.846E-05	3.146E-07	0.000E+00	2.093E-04	2.206E-04	1.596E-04	0.000E+00	2.569E-04	1.007E-03
Ni	3.101E-03	6.187E-03	6.488E-03	5.038E-03	2.012E-03	1.942E-03	3.187E-03	2.671E-03	3.005E-03	1.732E-03
Sr	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
Mn	6.515E-08	0.000E+00	0.000E+00	0.000E+00	2.254E-03	3.538E-03	4.655E-05	0.000E+00	4.565E-03	4.824E-07
Ca	1.595E-02	3.096E-02	3.245E-02	2.520E-02	1.012E-02	9.760E-03	1.594E-02	1.336E-02	1.505E-02	9.502E-03
K	3.069E-02	6.989E-02	7.386E-02	5.763E-02	2.632E-02	2.451E-02	5.094E-02	3.106E-02	3.951E-02	1.105E-02
Density (g/cc)	1.397E+00	1.840E+00	1.874E+00	1.674E+00	1.255E+00	1.218E+00	1.583E+00	1.349E+00	1.366E+00	1.181E+00
Void Frac.	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
wt.% H2O	5.153E+01	2.325E+01	2.089E+01	3.139E+01	6.465E+01	6.807E+01	3.815E+01	5.480E+01	5.276E+01	7.507E+01
TOC wt% C	8.391E-06	0.000E+00	0.000E+00	0.000E+00	2.959E-01	3.911E-01	5.289E-03	0.000E+00	4.950E-01	7.345E-05
free OH	0.000E+00	0.000E+00	0.000E+00	0.0 +00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00
OH	9.009E+00	1.980E+01	2.049E+01	115 +01	4.745E+00	3.510E+00	1.331E+01	7.968E+00	6.429E+00	4.171E+00
NO3	3.006E+00	4.891E+00	5.464E+00	4.4 +00	1.714E+00	1.534E+00	3.486E+00	2.818E+00	2.476E+00	1.197E+00
NO2	1.638E+00	4.485E+00	4.418E+00	3.225E+00	1.256E+00	1.131E+00	3.132E+00	1.336E+00	1.864E+00	7.840E-01
CO3	1.596E-02	3.096E-02	3.245E-02	2.520E-02	1.802E-01	2.263E-01	2.055E-02	1.336E-02	3.169E-01	9.550E-03

Table C.1. Summary of Chemical Tank Supernate/Salt Concentrations at Time of Leak (2 Sheets)

Tank	C-104	CY-107	CY-108	CY-109	CY-110	CY-111	CY-112	CY-113	CY-114	SX-115
Assumed Leak Date	1988	Ave. 64-67	Ave. 65-67	Ave. 64-67	1974	1973	1969	1962	1972	1964
Chemicals	(mo)	(mol/L)	(mol/L)	(mol/L)	(mol/L)	(mol/L)	(mol/L)	(mol/L)	(mol/L)	(mol/L)
PO4	5.792E-07	0.000E+00	0.000E+00	0.000E+00	1.140E-02	1.317E-02	4.138E-04	0.000E+00	1.791E-02	4.288E-06
SO4	3.206E-02	9.299E-02	9.229E-02	6.775E-02	9.641E-02	1.226E-01	6.646E-02	2.879E-02	1.714E-01	1.920E-02
Si (as SiO32-)	2.806E-02	9.803E-02	9.334E-02	6.561E-02	3.481E-02	3.425E-02	5.563E-02	2.229E-02	5.508E-02	1.279E-02
F	4.617E-07	0.000E+00	0.000E+00	0.000E+00	5.400E-03	5.272E-03	3.299E-04	0.000E+00	6.534E-03	3.418E-06
Cl	1.412E-01	3.215E-01	3.397E-01	2.651E-01	1.017E-01	8.848E-02	2.215E-01	1.429E-01	1.488E-01	5.071E-02
C6H5O7	4.771E-07	0.000E+00	0.000E+00	0.000E+00	1.810E-02	2.602E-02	3.408E-04	0.000E+00	3.548E-02	3.532E-06
EDTA	1.858E-08	0.000E+00	0.000E+00	0.000E+00	3.213E-04	4.655E-04	1.328E-05	0.000E+00	5.988E-04	1.376E-07
HEDTA	1.543E-08	0.000E+00	0.000E+00	0.000E+00	5.799E-04	9.256E-04	1.102E-05	0.000E+00	1.202E-03	1.142E-07
glycolate	6.734E-07	0.000E+00	0.000E+00	0.000E+00	3.077E-02	1.215E-02	4.811E-04	0.000E+00	3.811E-02	4.985E-06
acetate	6.989E-08	0.000E+00	0.000E+00	0.000E+00	2.233E-04	5.419E-05	4.993E-05	0.000E+00	3.255E-05	5.175E-07
oxalate	2.888E-14	0.000E+00	0.000E+00	0.000E+00	1.118E-09	1.738E-09	2.063E-11	0.000E+00	2.253E-09	2.138E-13
DBP	4.231E-07	0.000E+00	0.000E+00	0.000E+00	1.082E-02	1.686E-02	3.023E-04	0.000E+00	2.136E-02	3.133E-06
butanol	4.231E-07	0.000E+00	0.000E+00	0.000E+00	1.082E-02	1.686E-02	3.023E-04	0.000E+00	2.136E-02	3.133E-06
NH3	2.051E-02	1.122E-01	1.051E-01	7.226E-02	3.248E-02	3.205E-02	6.916E-02	2.123E-02	5.011E-02	1.305E-02
Fe(CN)6	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00	0.000E+00

Source: Jones et al. (2000a).

Note: This chart selects a single waste composition (from a single selected year or average of a range of years) for each tank that leaked. The objective is to provide the Tank Farm Vadose Zone Project with an unambiguous set of leak composition values. Data source is HDW model-SMM concentrations for selected tanks and for each year.

HDW = Hanford defined waste (model).

SMM = supernatant mixing model.

TOC = total organic compound.

Table C.2. Summary of Radionuclide Tank Supernate/Salt Concentrations at Time of Leak (3 Sheets)

Tank	S-104	SX-107	SX-108	SX-109	SX-110	SX-111	SX-112	SX-113	SX-114	SX-115
Assumed Leak Date	19	Ave. 64-67	Ave. 65-66	Ave. 64-67	1974	1973	1969	1962	19	
Radionuclides	(Ci)	(Ci/L)	(Ci/L)	(Ci/L)	(Ci/L)	(Ci/L)	(Ci/L)	(Ci/L)	(Ci)	
H-3	7.812E-05	6.640E-04	6.013E-04	3.960E-04	1.661E-04	1.531E-04	4.208E-04	8.092E-05	2.548E-04	7.551E-05
C-14	6.059E-06	3.044E-05	2.876E-05	1.996E-05	2.218E-05	2.942E-05	2.028E-05	6.264E-06	4.091E-05	3.657E-06
Ni-59	7.660E-07	3.543E-06	3.373E-06	2.361E-06	1.201E-06	1.418E-06	1.712E-06	7.828E-07	2.078E-06	4.413E-07
Ni-63	7.157E-05	3.475E-04	3.291E-04	2.290E-04	1.186E-04	1.403E-04	1.675E-04	7.309E-05	2.053E-04	4.315E-05
Co-60	2.420E-06	3.097E-05	2.744E-05	1.755E-05	2.491E-05	3.360E-05	1.961E-05	2.473E-06	4.646E-05	3.550E-06
Se-79	1.287E-06	5.756E-06	5.507E-06	3.878E-06	1.904E-06	1.984E-06	3.275E-06	1.330E-06	3.107E-06	7.007E-07
Str-90	4.961E-02	1.166E-01	1.225E-01	9.516E-02	5.514E-02	6.636E-02	6.020E-02	5.044E-02	9.720E-02	1.777E-02
Y-90	4.962E-02	1.166E-01	1.226E-01	9.519E-02	5.515E-02	6.638E-02	6.022E-02	5.046E-02	9.722E-02	1.777E-02
Zr-93	6.075E-06	2.853E-05	2.715E-05	1.900E-05	9.435E-06	9.899E-06	1.631E-05	6.278E-06	1.544E-05	3.455E-06
Nb-93m	4.963E-06	2.047E-05	1.977E-05	1.407E-05	6.690E-06	6.949E-06	1.154E-05	5.133E-06	1.090E-05	2.510E-06
Tc-99	4.247E-05	2.435E-04	2.272E-04	1.553E-04	1.593E-04	2.080E-04	1.602E-04	4.385E-05	2.912E-04	2.904E-05
Ru-106	1.820E-11	7.971E-09	6.766E-09	4.071E-09	4.222E-09	4.573E-09	4.831E-09	6.907E-12	7.089E-09	8.857E-10
Cd-113m	1.878E-05	1.334E-04	1.223E-04	8.175E-05	5.331E-05	5.863E-05	8.581E-05	1.935E-05	8.880E-05	1.570E-05
Sb-125	3.669E-06	1.158E-04	9.998E-05	6.166E-05	1.065E-04	1.452E-04	7.206E-05	3.631E-06	2.000E-04	1.307E-05
Sn-126	1.976E-06	8.667E-06	8.312E-06	5.868E-06	2.869E-06	2.979E-06	4.920E-06	2.044E-06	4.675E-06	1.054E-06
I-129	8.158E-08	4.604E-07	4.302E-07	2.945E-07	3.066E-07	4.016E-07	3.033E-07	8.423E-08	5.616E-07	5.496E-08
Cs-134	6.935E-08	7.004E-06	5.972E-06	3.617E-06	9.609E-07	4.299E-07	4.180E-06	6.248E-08	1.077E-06	7.764E-07
Cs-137	1.249E-01	8.378E-01	7.712E-01	5.185E-01	1.272E-01	5.765E-02	5.329E-01	1.288E-01	1.415E-01	9.885E-02
Ba-137m	1.182E-01	7.925E-01	7.296E-01	4.905E-01	1.204E-01	5.454E-02	5.042E-01	1.218E-01	1.339E-01	9.351E-02
Sm-151	4.591E-03	2.021E-02	1.937E-02	1.367E-02	6.685E-03	6.948E-03	1.148E-02	4.746E-03	1.090E-02	2.465E-03
Eu-152	4.539E-07	5.471E-06	4.860E-06	3.121E-06	2.014E-06	2.388E-06	2.600E-06	4.657E-07	3.527E-06	6.185E-07
Eu-154	5.843E-05	7.543E-04	6.680E-04	4.271E-04	3.916E-04	4.777E-04	4.733E-04	5.974E-05	6.919E-04	8.618E-05
Eu-155	2.150E-05	2.785E-04	2.466E-04	1.576E-04	1.160E-04	1.412E-04	1.323E-04	2.198E-05	2.057E-04	3.158E-05

Table C.2. Summary of Radionuclide Tank Supernate/Salt Concentrations at Time of Leak (3 Sheets)

Tank	S-104	SX-107	SX-108	SX-109	SX-110	SX-111	SX-112	SX-113	SX-114	SX-115
Assumed Leak Date	1965 (Ci/L)	Ave. 64-67 (Ci/L)	Ave. 65-66 (Ci/L)	Ave. 64-67 (Ci/L)	1974 (Ci/L)	1973 (Ci/L)	1969 (Ci/L)	1962 (Ci/L)	1972 (Ci/L)	1964 (Ci/L)
Radionuclides										
Ra-226	8.936E-11	2.125E-10	2.235E-10	1.735E-10	6.432E-11	6.273E-11	1.098E-10	9.199E-11	1.017E-10	2.893E-11
Ra-228	2.064E-12	9.465E-15	8.319E-15	5.265E-15	1.060E-08	4.447E-09	1.474E-09	6.165E-16	3.049E-09	1.528E-11
Ac-227	5.177E-10	1.234E-09	1.298E-09	1.008E-09	3.845E-10	3.764E-10	6.374E-10	5.341E-10	5.958E-10	1.657E-10
Pa-231	1.917E-09	6.197E-09	6.190E-09	4.567E-09	1.971E-09	2.053E-09	3.381E-09	1.986E-09	3.134E-09	7.760E-10
Th-229	1.631E-13	6.367E-13	5.954E-13	4.081E-13	2.714E-10	1.442E-10	3.554E-11	1.176E-13	1.075E-10	4.400E-13
Th-232	2.767E-13	2.681E-14	2.351E-14	1.483E-14	9.589E-10	7.156E-10	1.965E-10	1.635E-15	6.976E-10	2.039E-12
U-232	4.198E-11	6.790E-11	6.427E-11	4.481E-11	1.125E-07	1.272E-07	1.496E-08	1.449E-11	1.092E-07	1.808E-10
U-233	8.080E-11	1.721E-12	1.715E-12	1.266E-12	4.326E-07	4.899E-07	5.718E-08	5.523E-13	4.218E-07	5.933E-10
U-234	4.484E-07	8.120E-07	8.406E-07	6.458E-07	3.239E-07	3.572E-07	5.165E-07	3.297E-07	5.050E-07	3.818E-07
U-235	1.894E-08	3.188E-08	3.357E-08	2.623E-08	1.314E-08	1.460E-08	2.051E-08	1.419E-08	2.065E-08	1.473E-08
U-236	1.063E-08	4.325E-08	3.908E-08	2.572E-08	1.186E-08	1.202E-08	2.506E-08	5.216E-09	1.755E-08	2.257E-08
U-238	4.340E-07	6.400E-07	6.979E-07	5.629E-07	3.227E-07	3.424E-07	4.263E-07	3.365E-07	4.740E-07	2.823E-07
U-Total (M)	5.463E-03	8.064E-03	8.792E-03	7.089E-03	3.662E-03	4.149E-03	5.314E-03	4.234E-03	5.818E-03	3.558E-03
Np-237	2.765E-07	9.534E-07	9.424E-07	6.878E-07	5.653E-07	7.119E-07	6.576E-07	2.846E-07	1.011E-06	1.256E-07
Pu-238	2.491E-07	1.221E-06	1.121E-06	7.521E-07	7.478E-07	9.538E-07	5.906E-07	1.840E-07	1.358E-06	3.270E-07
Pu-239	1.567E-05	3.012E-05	3.163E-05	2.461E-05	2.267E-05	3.027E-05	1.560E-05	1.313E-05	4.187E-05	9.276E-06
Pu-240	2.265E-06	5.382E-06	5.436E-06	4.069E-06	4.002E-06	5.309E-06	2.731E-06	1.879E-06	7.383E-06	1.552E-06
Pu-241	1.399E-05	6.011E-05	5.611E-05	3.844E-05	5.033E-05	6.614E-05	2.938E-05	1.105E-05	9.275E-05	1.469E-05
Pu-242	6.017E-11	3.360E-10	3.086E-10	2.071E-10	2.825E-10	3.669E-10	1.620E-10	5.068E-11	5.195E-10	5.893E-11
Pu-Total (g/L)	2.622E-04	5.089E-04	5.335E-04	4.142E-04	2.509E-04	3.001E-04	2.621E-04	2.196E-04	4.331E-04	1.562E-04
Am-241	2.168E-05	8.798E-05	8.515E-05	6.073E-05	3.039E-05	3.018E-05	4.951E-05	2.239E-05	4.863E-05	1.093E-05
Am-243	2.033E-10	3.430E-09	3.008E-09	1.898E-09	1.159E-09	9.826E-10	1.814E-09	2.094E-10	1.753E-09	3.769E-10
Cm-242	1.034E-08	2.514E-07	2.183E-07	1.358E-07	7.703E-08	9.701E-08	8.209E-08	1.071E-08	1.414E-07	2.676E-08

Table C.2. Summary of Radionuclide Tank Supernate/Salt Concentrations at Time of Leak (3 Sheet)

Tank	S-104	SX-107	SX-108	SX-109	SX-110	SX-111	SX-112	SX-113	SX-114	SX-115
Assumed Leak Date	1965 (Ci/L)	Ave. 64-67 (Ci/L)	Ave. 65-66 (Ci/L)	Ave. 64-67 (Ci/L)	1974 (Ci/L)	1973 (Ci/L)	1969 (Ci/L)	1962 (Ci/L)	1972 (Ci/L)	1964 (Ci/L)
Radionuclides										
Cm-243	2.370E-10	2.490E-08	2.124E-08	1.288E-08	7.487E-09	9.285E-09	8.166E-09	2.455E-10	1.365E-08	2.598E-09
Cm-244	7.224E-09	2.482E-07	2.141E-07	1.319E-07	8.013E-08	9.639E-08	8.123E-08	7.484E-09	1.455E-07	2.621E-08

Note: This chart selects a single waste composition (from a single selected year or average of a range of years) for each tank that leaked.

Objective is to provide the Tank Farm Vadose Zone Project with an unambiguous set of leak composition values.

Data source (HDW model-SMM Concentrations for selected tanks and for each year).

HDW = Hanford defined waste (model).

SMM = supernatant mixing model.

Once developed, waste compositions can be coupled with leak volumes to develop specific leak inventory estimates. However, published leak volume estimates (Hanlon 2001) are highly uncertain for a number of the SX tank farm leaks (Jones et al. 2000a). Thus, it was necessary to use other data sources to develop leak volume estimates. This process is discussed in the following sections.

C.3.2 GAMMA LOGGING DATA

Since the early 1960s gamma logging data have been used as a secondary tank leak monitoring system (Isaacson and Gasper 1981). In practice, strategically placed shallow boreholes (24.4 to 45.7 m [80 to 150 ft] below ground surface [bgs]), called 'drywells,' were routinely monitored for changes in total gamma activity. Hence, the activity is known as gross gamma logging. Drywells were located approximately 3.1 m (10 ft) from the tanks and generally 4 to 8 drywells surrounded each 'active' tank (that is, leak monitoring concentrated on tanks currently being used to store liquid wastes). Tanks known to have leaked (e.g., tank SX-113) where all pumpable liquids had been removed, were not given high priority to be monitored for additional leakage. For additional leak monitoring capability, 10 of the 15 tanks in the SX tank farm had laterals (i.e., horizontal pipes radiating from a central caisson) installed approximately 3.0 m (10 ft) below the base of the tank. Except for tank SX-113, each tank had three laterals radiating from a nearby caisson. As the prototype for the laterals tank leak monitoring system, tank SX-113 had five laterals installed under it.

During the routine gamma logging program, changes in gamma activity in a borehole would suggest potential leakage from a nearby waste storage tank. Although the gross gamma logging data were stored electronically from 1974 to the end of the logging program in 1994, data comparisons within any specific drywell were restricted to short time intervals. Gross gamma logging data were treated as being of value only for 'real-time' leak monitoring of active single-shell tanks (SSTs).

As part of the WMA S-SX vadose zone characterization, historic gross gamma logging data are assessed in Myers (1999a), and Myers (1999b). Although the gamma logging instrumentation underwent major modifications (particularly the probes) over the 20 years of data collection, the data exhibited surprising reproducibility. The data analysis also provided useful information about the potential movement of gamma emitting radionuclides over the 20-year period.

The validity of gross gamma logging methodology as a tank leak detection system was critically evaluated in *A Scientific Basis for Establishing Dry-Well Monitoring Frequencies* (Isaacson and Gasper 1981). One of the conclusions from the evaluation was that the gross gamma data provided far more insight into the migration of radionuclides in the soil than it did about potential leaks in active tanks. With the passage of time and thus decay of the short-lived mobile gamma emitting radionuclides such as ruthenium-106, the 1981 conclusions are more valid than ever.

In 1994, a baseline spectral gamma-logging program was initiated to assess the nature and extent of gamma emitting radionuclides in the tank farms vadose zone (DOE-GJPO 1995a, 1995b, 1995c; DOE-RL 1996a) by using the unique radiation emitted to identify and quantify the radionuclides. Essentially all existing drywells within each tank farm were logged with a system

designed to provide specific isotopic composition of gamma emitting radionuclides. Baseline spectral gamma logging results were published for each tank farm. The gamma-logging probe selected for the initial logging runs became saturated at approximately 1,000 pCi/g of cesium-137. Thus, in the most highly contaminated zones, quantitative values were not determined. At a later date the highly contaminated zones were re-logged using a less sensitive probe and updated results were published in supplemental tank farm reports. Ninety-eight drywells were logged in the SX tank farm and results were published in *Vadose Zone Characterization Project at the Hanford Tank Farms, SXTank Farm Report* (DOE-GJPO 1996) and its supplement, *Addendum to the SX Tank Farm Report* (DOE-GJPO 2000). Seventy-two drywells were logged in the S tank farm and results were published in DOE-GJPO (1998) and its supplement, *Addendum to the S Tank Farm Report* (DOE-GJO 2000).

The baseline spectral gamma-logging program has made major contributions to the current tank farm vadose zone characterization efforts. The main radionuclide found was cesium-137. Only very small amounts (i.e., a few pCi/g) of cobalt-60 and/or europium-154 were found in the S and SX tank farm drywells.

C.3.3 KFUGING ANALYSIS

The SX tank farm gamma logging and soil analysis data for cesium-137 represent 'point measurements' along a vertical, horizontal, or slant direction. The goal of kriging analysis of the cesium-137 data was to establish mathematically defensible inventory estimates associated with the gamma contamination around each tank in the SX farm. Two separate data analyses were conducted. The first, conducted by Professor Dan Goodman, Montana State University (MSU) beginning in 1998, combined *gross* gamma and spectral gamma logging data with soil analysis data from borehole 41-09-39 and historical soils data (Raymond and Shdo 1966) (Goodman 2000). The MSU results are referred to as 'MSU kriging results' in this document. The second statistical analysis of the SX tank farm cesium-137 data, conducted by HydroGeologic, Inc. (HGL) (Sullivan et al. 2001), began with the same data set as used by MSU but also included newly acquired soils analysis data from the SX-108 slant borehole (Serne 2001d) and the updated spectral gamma logging results (DOE-GJPO 2000b).

The MSU statistical analysis focused on two objectives.

- The gross gamma logging data were evaluated to establish calibration curves so as to use the gross gamma data to develop 'datapatches' for the regions of the spectral gamma data set lost because of detector saturation in the initial spectral gamma logging.
- The resulting enhanced gamma logging-based cesium-137 data set was coupled with soils analysis data to develop cesium-137 inventory estimates for the regions around each tank in the SX farm.

The projected cesium-137 inventory estimate for each of tank in the SX tank farm is listed in Table C.3. Inventory estimates are reported at both the 50 and 95 percentiles.

**Table C.3. SX Tank Farm Cesium-137 Inventory
Estimates from Kriging Analyses**

Tank	MSU 50% (pCi)	MSU 95% (pCi)	HGL 50% (pCi)
sx-101	9.1E+09	2.1E+10	2.3E+10
sx-102	0.0E+00	0.0E+00	1.5E+10
SX-103	0.0E+00	0.0E+00	2.1E+10
SX-104	2.7E+08	1.6E+09	7.7E+09
SX-105	5.5E+09	1.3E+10	1.3E+10
SX-106	0.0E+00	0.0E+00	5.9E+09
SX-107	8.0E+15	1.5E+16	4.2E+16
sx-108	1.4E+16	3.6E+16	3.9E+16
sx-109	7.2E+14	2.3E+15	1.6E+15
SX-110	2.0E+12	1.3E+13	7.5E+12
SX-111	2.3E+11	1.1E+12	2.3E+11
sx-112	1.8E+13	9.5E+13	2.9E+13
SX-113	0.0E+00	0.0E+00	6.4E+07
SX-114	0.0E+00	0.0E+00	1.9E+08
SX-115	N/R	N/R	1.1E+14

HGL = HydroGeologic, **Inc.**

MSU = Montana State **University.**

N/R = not **reported.**

The second kriging analysis was focused on understanding the impact of the addition of the cesium-137 soils analysis data from the SX-108 slant borehole investigation on the overall cesium-137 inventory estimate. **Also** included in the second kriging analysis were the updated spectral gamma logging data for cesium-137 from highly contaminated zones (DOE-GJPO 2000b). Thus, the data patches from historical gross gamma data developed by MSU for that kriging analysis were not required for the HGL kriging analysis.

The first step in any kriging process is the development of a variogram model. Vertical and horizontal correlation lengths are determined during the variogram analysis. Significantly different Correlation lengths were reported between the two kriging analyses.

- MSU variogram analysis led to a horizontal correlation length of 8.2 m (26.9 ft) and a vertical correlation length of 3 m (10 ft)
- HGL variogram analysis led to horizontal and vertical correlation lengths of 15 m (49 ft) and 20 m (66 ft), respectively.

The practical result of longer correlation lengths is the projection of somewhat larger plume volumes with the existing data set.

There are a number of reasons for the large correlation lengths reported in the HGL kriging analysis (Sullivan et al. 2001). The most obvious reason is the addition of the cesium-137 concentrations along the SX-108 slant borehole, giving much better definition of the vertical contamination directly below tank SX-108. However, there were also differences in approach. The MSU variogram analysis treated all of the available data within the SX tank farm while the HGL variogram analysis focused on the area around tank SX-108. The decision to estimate correlation lengths using data only from around tank SX-108 focused the analysis in the area where the maximum amount of data was available. The correlation lengths derived from the analysis of data around tank SX-108 were then used in the kriging analysis for all of the SX tank farm data. The intent was to apply the knowledge gained from detailed field investigations around tank SX-108 to the contamination found around and under other SX farm tanks.

This was justified because very similar waste types leaked from all failed SX farm tanks and the geology was assumed reasonably similar across the SX tank farm. The HGL kriging analysis also reports results of sensitivity studies associated with data processing decisions.

The cesium-137 inventory estimates developed in the HGL kriging analysis are also listed by tank in Table C.3. An example of the graphical representation of cesium-137 activity generated in the HGL kriging analysis is shown in Figures C.1 through C.7. This series of figures provide a graphical representation of the projected cesium-137 contamination as a function of activity levels.

The comparison between projected cesium-137 inventory estimates for each tank in the SX tank farm is shown in Figure C.8.

There are subjective decisions that are made in any statistical analysis involving large and diverse data sets such as those reported here where data compression is required. The HGL kriging analysis explored potential impacts of these decisions on reported results. The HGL analysis results are discussed briefly in the following paragraphs.

Both kriging analyses were forced to reduce the size of the data set prior to computations because the data set was too large to be processed with available computer systems. Both groups separated the tank farm area into a 1 m by 1 m grid size. MSU used a 1 m depth to form 1 m³ sections. The geometric mean of all cesium-137 concentration values with the 1 m³ was assigned to the center of the cube. The variogram analysis and kriging were completed with this reduced data set. The HGL data process approach was quite similar except the grid size was 1 m (3 ft) by 1 m (3 ft) by 0.5 m (1.5 ft) depth.

The geometric mean is commonly used as an approach for compressing large environmental data sets, where values span multiple orders of magnitudes (e.g., HGL data in the SX tank farm). However, other approaches could be taken. For example, a more conservative approach would be to assign the data value of the volume space as the maximum value reported within that grid volume. Or, one might chose to use the arithmetic mean. Results of the three data compression alternatives are shown in Figure C.9 for tank SX-107. A more detailed comparison between 'geometric mean' and 'maximum' values for all SX farm tanks are shown in Tables C.4 and C.5 (Sullivan et al. 2001).

Figure C.1. Three-Dimensional Perspective of Cesium-137
Contaminated Soil Above 5×10^1 pCi/g

Figure C.2. Three-Dimensional Perspective of Cesium-137
Contaminated Soil Above 5×10^2 pCi/g

Figure C.3. Three-Dimensional Perspective of Cesium-137
Contaminated Soil Above 5×10^3 pCi/g

Figure C.4. Three-Dimensional Perspective of Cesium-137
Contaminated Soil Above 5×10^4 pCi/g

Figure C.5. Three-Dimensional Perspective of Cesium-137
Contaminated Soil Above 5×10^5 pCi/g

Figure C.6. Three-Dimensional Perspective of Cesium-137
Contaminated Soil Above 5×10^6 pCi/g

**Figure C.7. Three-Dimensional Perspective of Cesium-137
Contaminated Soil Above 5×10^7 pCi/g**

Figure C.8. Total Pico-Curies of Cesium-137 Inventory by Tank

Figure C.9. Estimated Activity Levels and Estimated Contaminated Soil Volume Using Max, Mean, and Geometric Mean Sample Data Filtering for Tank SX-107

**Table C.4. Summary of Activity and Volume Estimates by Tank
and Activity Threshold with Geometric Mean Filtering**

Tank	Activity/ Volume	Activity Threshold							
		5 (pCi/g)	50 (pCi/g)	500 (pCi/g)	5,000 (pCi/g)	50,000 (pCi/g)	500,000 (pCi/g)	5E+06 (pCi/g)	5E+07 (pCi/g)
SX-101	Activity (pCi)	2.30E+10	4.11E+09	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Volume (m ³)	1.10E+03	2.05E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SX-102	Activity (pCi)	1.53E+10	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Volume (m ³)	1.14E+03	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SX-103	Activity (pCi)	2.12E+10	2.24E+08	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Volume (m ³)	1.31E+03	2.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SX-104	Activity (pCi)	7.75E+09	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Volume (m ³)	5.23E+02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SX-105	Activity (pCi)	1.33E+10	7.62E+08	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Volume (m ³)	1.03E+03	3.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SX-106	Activity (pCi)	5.90E+09	3.35E+08	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Volume (m ³)	4.93E+02	2.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SX-107	Activity (pCi)	4.22E+16	4.22E+16	4.22E+16	4.22E+16	4.22E+16	4.20E+16	4.06E+16	3.32E+16
	Volume (m ³)	7.82E+03	4.33E+03	2.90E+03	2.00E+03	1.36E+03	8.05E+02	3.57E+02	1.18E+02
SX-108	Activity (pCi)	3.91E+16	3.91E+16	3.91E+16	3.91E+16	3.90E+16	3.86E+16	3.55E+16	6.20E+15
	Volume (m ³)	1.83E+04	1.07E+04	7.02E+03	4.69E+03	3.06E+03	1.82E+03	9.02E+02	5.35E+01
SX-109	Activity (pCi)	1.56E+15	1.56E+15	1.56E+15	1.55E+15	1.48E+15	1.13E+15	2.20E+14	0.00E+00
	Volume (m ³)	1.74E+04	1.04E+04	6.58E+03	3.69E+03	1.58E+03	3.81E+02	1.55E+01	0.00E+00
SX-110	Activity (pCi)	7.51E+12	7.50E+12	7.47E+12	7.30E+12	6.63E+12	3.88E+12	0.00E+00	0.00E+00
	Volume (m ³)	5.15E+02	2.05E+02	9.10E+01	3.50E+01	1.20E+01	3.00E+00	0.00E+00	0.00E+00
SX-111	Activity (pCi)	2.26E+11	1.91E+11	1.07E+11	2.97E+10	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Volume (m ³)	1.72E+03	3.42E+02	4.90E+01	1.50E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SX-112	Activity (pCi)	2.92E+13	2.91E+13	2.87E+13	2.67E+13	2.05E+13	7.45E+12	0.00E+00	0.00E+00
	Volume (m ³)	7.14E+03	2.27E+03	9.53E+02	2.82E+02	5.35E+01	6.00E+00	0.00E+00	0.00E+00
SX-113	Activity (pCi)	6.41E+07	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Volume (m ³)	6.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SX-114	Activity (pCi)	1.90E+08	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Volume (m ³)	1.25E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SX-115	Activity (pCi)	1.14E+14	1.14E+14	1.14E+14	1.13E+14	1.07E+14	9.27E+13	5.50E+13	0.00E+00
	Volume (m ³)	4.24E+03	1.46E+03	6.12E+02	2.46E+02	6.70E+01	1.70E+01	3.00E+00	0.00E+00
SX Tank Farm Totals	Activity (pCi)	8.3011E+16	8.3011E+16	8.3011E+16	8.2997E+16	8.2814E+16	8.1834E+16	7.6375E+16	3.940E+16
	Volume (m ³)	62,750	29,375	18,205	10,945	6,133	3,032	1,278	172

**Table C.5. Summary of Activity and Volume Estimates by Tank
and Activity Threshold with Maximum Value Filtering**

Tank	Activity/ Volume	Activity Threshold Level							
		5 (pCi/g)	50 (pCi/g)	500 (pCi/g)	5,000 (pCi/g)	50,000 (pCi/g)	500,000 (pCi/g)	5E+06 (pCi/g)	5E+07 (pCi/g)
SX-101	Activity (pCi)	6.29E+10	1.54E+10	1.96E+09	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Volume (m ³)	2.56E+03	7.55E+01	1.50E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SX-102	Activity (pCi)	5.62E+10	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Volume (m ³)	3.19E+03	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SX-103	Activity (pCi)	7.60E+10	9.26E+09	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Volume (m ³)	3.50E+03	6.80E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SX-104	Activity (pCi)	3.61E+10	1.53E+09	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Volume (m ³)	1.74E+03	1.30E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SX-105	Activity (pCi)	7.03E+10	1.19E+10	9.85E+09	4.77E+09	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Volume (m ³)	3.66E+03	1.25E+01	2.50E+00	5.00E-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SX-106	Activity (pCi)	5.71E+10	5.78E+09	4.03E+09	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Volume (m ³)	3.09E+03	1.05E+01	2.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SX-107	Activity (pCi)	8.08E+16	8.08E+16	8.08E+16	8.08E+16	8.08E+16	8.05E+16	7.86E+16	6.44E+16
	Volume (m ³)	9.94E+03	5.22E+03	3.54E+03	2.52E+03	1.79E+03	1.19E+03	6.38E+02	2.12E+02
SX-108	Activity (pCi)	5.02E+16	5.02E+16	5.02E+16	5.02E+16	5.01E+16	4.96E+16	4.60E+16	9.84E+15
	Volume (m ³)	2.27E+04	1.16E+04	7.60E+03	5.24E+03	3.51E+03	2.14E+03	1.08E+03	8.15E+01
sx-109	Activity (pCi)	3.77E+15	3.77E+15	3.77E+15	3.76E+15	3.67E+15	3.06E+15	9.61E+14	0.00E+00
	Volume (m ³)	2.19E+04	1.26E+04	8.33E+03	5.20E+03	2.68E+03	8.49E+02	6.60E+01	0.00E+00
sx-110	Activity (pCi)	1.11E+14	1.11E+14	1.11E+14	1.10E+14	1.09E+14	1.04E+14	8.35E+13	0.00E+00
	Volume (m ³)	1.50E+03	2.83E+02	1.37E+02	6.50E+01	3.00E+01	1.15E+01	4.00E+00	0.00E+00
SX-111	Activity (pCi)	1.16E+12	1.08E+12	9.70E+11	4.52E+11	1.11E+11	0.00E+00	0.00E+00	0.00E+00
	Volume (m ³)	4.16E+03	5.92E+02	1.79E+02	1.65E+01	5.00E-01	0.00E+00	0.00E+00	0.00E+00
SX-112	Activity (pCi)	6.16E+13	6.14E+13	6.07E+13	5.82E+13	4.82E+13	2.76E+13	0.00E+00	0.00E+00
	Volume (m ³)	1.21E+04	3.50E+03	1.26E+03	4.57E+02	8.90E+01	1.30E+01	0.00E+00	0.00E+00
SX-113	Activity (pCi)	8.42E+08	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Volume (m ³)	7.00E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Activity (pCi)	6.16E+09	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
SX-115	Activity (pCi)	2.69E+14	2.69E+14	2.69E+14	2.68E+14	2.60E+14	2.27E+14	1.46E+14	0.00E+00
	Volume (m ³)	5.30E+03	1.82E+03	8.27E+02	3.97E+02	1.54E+02	3.80E+01	6.00E+00	0.00E+00
SXTank Farm	Activity (pCi)	1.35E+17	1.35E+17	1.35E+17	1.35E+17	1.35E+17	1.34E+17	1.26E+17	7.43E+16

C.3.4 INVENTORY ESTIMATES FOR WASTE MANAGEMENT AREA S-SX TANK LEAKS

Leak volume estimates and projected inventory estimates for WMA S-SX tank leaks are listed in Tables C.6 and C.7 (Jones et al. 2000a). Leak inventory estimates for tanks SX-107, SX-108, and SX-109 were based on cesium-137 inventories developed by the MSU kriging analysis (Goodman 2000). Leak volumes for these three tanks were estimated from cesium-137 inventory estimates (Goodman 2000) coupled with waste composition estimates (see Section C.3.1). Inventory estimates for tanks S-104, SX-113, and SX-115 were based on documented leak volumes (Hanlon 2001; Jones et al. 2000a). For these three cases, leak volumes were combined with tank waste inventory estimates (see Section C.3.1) to develop inventory estimates for each tank leak.

The following discussion focuses on potential modifications to the published WMA S-SX inventory estimates based on the updated HGL kriging results.

Inventory and leak volume estimates developed in Jones et al. (2000a) are listed in Tables C.6 and C.7. The estimates were made using the waste tank compositions (discussed in Section C.3.1) and the leak volumes as estimated from the cesium-137 inventory in the soil (discussed in Section C.3.3). The inventory estimates shown in Tables C.6 and C.7 for tanks SX-107, SX-108, and SX-109 were developed using 95 percentile cesium-137 data from MSU (Goodman 2000). That is, these inventory estimates were biased high by using the 95 percentile data rather than the mean or 50 percentile values. The decision to use the higher values was driven by an assumption that the cesium-137 plume estimates failed to reflect realistic estimates of the cesium-137 inventories directly below the tanks. (This was one of the conclusions discussed in the MSU report [Goodman 2000] and was used as one of the technical justifications for drilling the SX-108 slant borehole.)

Those estimates remain as reasonable estimates for use in leak impact assessment studies. The HGL kriging analysis was more robust than the MSU efforts because only experimentally determined measurements were used by HGL, and HGL correlation lengths were based on a single tank (i.e., tank SX-108) where the most data were available then applied to all SX farm tanks.

The inventory estimates for tanks SX-107, SX-108, and SX-109 were developed using the 95 percentile MSU kriging data. If the HGL kriging results had been used in developing the inventory estimates, the values for tanks SX-108 and SX-109 listed in Tables C.6 and C.7 would have changed very little. However, the tank SX-107 inventory estimates would have been slightly higher than those reported for tank SX-108 in Tables C.6 and C.7. Leak inventory estimates for tanks S-104, SX-113, and SX-115 were based on historical leak volumes. Leak volumes from tanks SX-113 and SX-115 are well documented (Hanson et al. 1962; Raymond and Shdo 1966) whereas the leak volume from tank S-104 is significantly more uncertain. The 24,000 gal (91,000 L) leak volume currently reported in *Waste Tank Summary Report for Month Ending March 31, 2001* (Hanlon 2001) for tank S-104 is based on long-term liquid level decreases (Agnew et al. 1997). However, the waste footprint projected from field investigations using cone penetrometer techniques and spectral gamma logging data fail to document the inventory estimates shown in Tables C.6 and C.7 for tank S-104. Thus, the tank S-104 inventory estimates listed in Tables C.6 and C.7 are conservative.

**Table C.6. Estimated Inventory Lost to Vadose Zone
in the S and SX Tank Farms (2 Sheets)**

Chemical	Estimated S-104 Inventory Loss (kg)	Estimated SX-107 Inventory Loss (kg)	Estimated sx-108 Inventory Loss (kg)	Estimated SX-109 Inventory Loss (kg)	Estimated SX-113 Inventory Loss (kg)	Estimated SX-115 Inventory Loss (kg)
Leak Vol.	24,000 gal ^a	63,500 gal ^b	15,200 gal ^b	989 gal ^b	15,000 gal ^a	50,000 gal ^a
Na	1.82E+04	9.90E+03	37E+	1.54E+03	1.05E+04	1.57E+04
Al3	3.83E+03	2.00E+03	4.78E+03	3.11E+02	1.95E+03	4.24E+03
Fe (Total)	1.81E+01	8.87E+00	2.12E+01	1.38E+00	9.47E+00	2.25E+01
Cr	7.81E+02	4.71E+02	1.13E+03	7.33E+01	5.08E+02	5.03E+02
Bi	1.71504	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.63E-03
La	2.79E-10	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.31E-09
Hg	6.49E-02	1.90E-04	4.54E-04	2.95E-05	0.00E+00	2.40E-01
ZrO(OH)2	1.15E-05	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.77E-04
Pb	1.07E+01	3.13E-02	7.48E-02	4.87E-03	0.00E+00	3.96E+01
Ni	1.66E+01	8.36E+00	2.00E+01	1.30E+00	8.94E+00	1.93E+01
Sr	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Mn	3.27E-04	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.04E-03
Ca	5.82E+01	2.85E+01	6.82E+01	4.44E+00	3.05E+01	7.22E+01
K	1.09E+02	6.33E+01	1.52E+02	9.86E+00	6.92E+01	8.21E+01
U-Total	1.19E+02	4.58E+01	1.10E+02	7.14E+00	5.74E+01	1.61E+02
Pu-Total	2.39E-02	1.17E-02	2.80E-02	1.82E-03	1.25E-02	2.97E-02
TOC wt% C	1.28E+02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
free OH	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
OH	1.40E+04	7.66E+03	1.83E+04	1.19E+03	7.72E+03	1.35E+04
NO3	1.70E+04	7.40E+03	1.77E+04	1.15E+03	9.96E+03	3.87E+03
NO2	6.87E+03	4.49E+03	1.07E+04	6.99E+02	3.50E+03	9.23E+03
C03	8.73E+01	4.28E+01	1.02E+02	6.66E+00	4.57E+01	8.35E+01
PO4	5.02E-03	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.89E-02
SO4	2.81E+02	1.95E+02	4.68E+02	3.04E+01	1.58E+02	3.46E+02
Si (as SiO32-)	1.94E+02	1.57E+02	3.76E+02	2.45E+01	9.66E+01	2.33E+02
F	8.00E-04	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.94E-02
Cl	4.57E+02	2.65E+02	6.33E+02	4.12E+01	2.89E+02	1.83E+02
C6H5O7	8.22E-03	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.27E-01
EDTA	1.69E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.32E-03
HEDTA	1.41E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.75E-03
acetateE-	6.37E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.80E-03
oxalate	2.63E-12	0.00E+00	0.00E+00	0.00E+00	0.00E+00	3.58E-09

**Table C.6. Estimated Inventory Lost to Vadose Zone
in the S and SX Tank Farms (2 Sheets)**

Chemical	Estimated S-104 Inventory Loss (kg)	Estimated SX-107 Inventory Loss (kg)	Estimated sx-108 Inventory Loss (kg)	Estimated sx-109 Inventory Loss (kg)	Estimated SX-113 Inventory Loss (kg)	Estimated SX-115 Inventory Loss (kg)
Leak Vol.	24,000 gal ^a	63,500 gal ^b	15,200 gal ^b	989 gal ^b	15,000 gal ^a	50,000 gal ^a
DBP	3.86E-05	0.00E+00	0.00E+00	0.00E+00	.00E+00	9.58E-02
butanol	3.86E-05	0.00E+00	0.00E+00	0.00E+00	.00E+00	1.40E-02
NH ₃	1.87E+00	3.96E+01	9.48E+01	6.17E+00	06E+01	4.21E+01
Fe(CN) ₆	0.00E+00	0.00E+00	0.00E+00	0.00E+00	00E+00	0.00E+00

^aLeak volumes from Hutton (2001).

^bLeak volumes estimated from Montana State University kriging analysis of gamma logging data (Goodman 2000).

**Table C.7. Estimated Inventory Lost to Vadose Zone
in the S and SX Tank Farms (Radionuclides) (2 Sheets)**

Radionuclide	Estimated S-104 Inventory Loss Ci	Estimated SX-107 Inventory Loss Ci	Estimated SX-108 Inventory Loss Ci	Estimated sx-109 Inventory Loss Ci	Estimated SX-113 Inventory Loss Ci	Estimated SX-115 Inventory Loss Ci
H-3	7.12E+00	1.34E+01	3.20E+01	2.08E+00	4.61E+00	1.43E+01
C-14	5.53E-01	6.37E-01	1.52E+00	9.92E-02	3.57E-01	6.95E-01
Ni-59	6.99E-02	7.46E-02	1.79E-01	1.16E-02	4.46E-02	8.38E-02
Ni-63	6.53E+00	7.28E+00	1.74E+01	1.13E+00	4.17E+00	8.20E+00
Co-60	2.21E-01	6.11E-01	1.46E+00	9.52E-02	1.41E-01	6.74E-01
Se-79	17E-01	1.22E-01	2.92E-01	1.90E-02	7.58E-02	1.33E-01
Sr-90	52E+03	2.69E+03	6.44E+03	4.19E+02	2.88E+03	3.38E+03
Y-90	4.53E+03	2.69E+03	4E+03	4.19E+02	2.88E+03	3.38E+03
Zr-93	5.54E-01	6.01E-01	4E+00	9.36E-02	3.58E-01	6.56E-01
Nb-93m	4.53E-01	4.01E-01	1.05E+00	6.80E-02	2.93E-01	4.77E-01
Tc-99	1.87E+00	5.03E-01	1.21E+01	7.84E-01	2.50E+00	5.52E+00
Ru-106	1.66E-06	1.51E-04	3.62E-04	2.36E-05	3.94E-07	1.68E-04
Cd-113m	1.71E+00	2.71E+00	6.50E+00	4.23E-01	1.10E+00	2.98E+00
Sb-125	3.35E-01	2.23E+00	5.34E+00	3.48E-01	2.07E-01	2.48E+00
Sn-126	1.80E-01	1.84E-01	4.40E-01	2.86E-02	1.16E-01	2.00E-01
I-129	7.44E-03	9.53E-03	2.28E-02	1.48E-03	4.80E-03	1.04E-02
Cs-134	6.32E-01	1.33E-01	3.19E-01	2.08E-02	3.56E-03	1.48E-01
ICs-137	1.14E+04	1.71E+04	4.10E+04	2.67E+03	7.34E+03	1.88E+04
Ba-137m	08E+04	1.62E+04	3.87E+04	2.52E+03	6.94E+03	1.78E+04
Sm-151	19E+02	4.28E+02	1.03E+03	6.67E+01	2.71E+02	4.68E+02
Eu-152	4.14E-02	1.08E-01	2.59E-01	1.69E-02	2.65E-02	1.18E-01
Eu-154	5.33E+00	1.49E+01	3.56E+01	2.32E+00	3.41E+00	1.64E+01
Eu-155	1.96E+00	5.49E+00	1.31E+01	8.55E-01	1.25E+00	6.00E+00
Ra-226	8.15E-06	4.90E-06	1.17E-05	7.64E-07	4E-07	5.50E-07
Ra-228	1.88E-07	1.85E-10	4.44E-10	2.89E-11	3.51E-11	2.90E-06
Ac-227	4.72E-05	2.85E-05	6.81E-05	4.43E-06	3.04E-05	3.15E-05
Pa-231	1.75E-04	1.36E-04	3.26E-04	2.12E-05	1.13E-04	1.47E-04
Th-229	1	1	3.16E-08	2.05E-09	6.70E-09	8.36E-08
Th-232	2.52E-08	5.24E-10	1.25E-09	8.16E-11	9.32E-11	3.87E-07
U-232	3.83E-06	1.42E-06	3.41E-06	2.22E-07	8.26E-07	3.44E-05
U-233	7.37E-06	3.78E-08	9.05E-08	5.89E-09	3.15E-08	1.13E-04
U-234	4.09E-02	1.85E-02	4.43E-02	2.88E-03	1.88E-02	7.25E-02
U-235	1.73E-03	7.37E-04	1.77E-03	1.15E-04	8.09E-04	2.80E-03
U-236	9.69E-04	8.69E-04	2.08E-03	1.35E-04	2.97E-04	4.29E-03

**Table C.7. Estimated Inventory Lost to Vadose Zone
in the S and SX Tank Farms (Radionuclides) (2 Sheets)**

Radionuclide	Estimated S-104 Inventory Loss Ci	Estimated SX-107 Inventory Loss Ci	Estimated SX-108 Inventory Loss Ci	Estimated SX-109 Inventory Loss Ci	Estimated SX-113 Inventory Loss Ci	Estimated SX-115 Inventory Loss Ci
U-238	3.96E-02	1.53E-02	3.66E-02	2.38E-03	1.92E-02	5.36E-02
Np-237	2.52E-02	2.08E-02	4.97E-02	3.24E-03	1.62E-02	2.39E-02
Pu-238	2.27E-02	2.49E-02	5.96E-02	3.87E-03	1.05E-02	6.21E-02
Pu-239	1.43E+00	6.95E-01	1.66E+00	3E-01	7.48E-01	1.76E+00
Pu-240	2.07E-01	1.20E-01	2.87E-01	1.86E-02	1.07E-01	2.95E-01
Pu-241	1.28E+00	1.24E+00	2.98E+00	1.94E-01	6.30E-01	2.79E+00
Pu-242	5.49E-06	6.85E-06	1.64E-05	7E-06	2.89E-06	1.1E-05
Am-241	1.98E+00	1.88E+00	4.50E+00	2.93E-01	1.28E+00	2.08E+00
Am-243	1.85E-05	6.70E-05	1.60E-04	1.04E-05	1.19E-05	7.16E-05
Cm-242	9.43E-04	4.87E-03	1.17E-02	7.59E-04	6.11E-04	5.0E-04
Cm-243	3E-04	4.75E-04	1.14E-03			
Cm-244	6.59E-04	4.78E-03	1.14E-02	7.44E-04	4.27E-04	4.98E-03

C.3.5 SPECIATION ANALYSIS

Significant quantities of high-level waste (HLW) were lost to the soil column from large underground tanks in WMA S-SX during long-term storage of the wastes produced in the Reduction-Oxidation (REDOX) Plant. **An** understanding of the mechanisms of soil/waste reactions controlling the movement of tank waste through the vadose zone requires knowledge of waste components on a molecular level. However, **this** level of tank waste chemistry is generally not available since this level of understanding was not required for the original plant operations or for long-term storage and waste management. *REDOX Technical Manual* (GE 1951) and the updated flowsheets from *Standard Inventories of Chemicals and Radionuclides in Hanford Site Tank Wastes* (Kupfer et al. 1998) provide clear guidance **as** to the conditions required for successful operations of separations process but only limited understanding of the underlying fundamental chemistry. Thus, the most practical approach for developing an understanding of the chemical species present in leaked tank waste comes from a chemical equilibria-based computer model that develops speciation of bulk waste components.

Chemical thermodynamic-based models of aqueous systems can be applied to predict reaction products if the controlling thermodynamic parameters are sufficiently well understood. However, the tank waste mixtures are extremely complex and many of the required thermodynamic parameters are only poorly understood. Any thermodynamic-based modeling exercise involving a tank waste matrix requires many approximations and assumptions. Thus, speciation modeling results must be treated with considerable caution.

The initiative was to conduct preliminary scoping studies using the Environmental Simulation Program (ESP), a thermodynamic-based chemical process simulator that has been widely applied at the Hanford Site (MacLean and Eager 1998). ESP is currently used to simulate transfers, mixing, and treatment of tank wastes for both the waste feed delivery project and vitrification pretreatment. It has been used to simulate processing of plutonium solutions, the clean salt waste treatment process, sluicing of tank wastes, and other nuclear-waste related processing.

The ESP is designed to model the processing of complex, concentrated aqueous solutions, organic liquids, solids, and vapors. It uses sophisticated thermodynamic models to predict the activity coefficients and equilibrium constants of most species and equilibrium relationships that can exist in tank wastes, or during processing of plant wastes. It can be used to calculate the equilibrium or time dependent composition of mixtures of solids, liquids, and gases.

The ESP calculates the thermodynamic equilibrium of all phases by minimizing the chemical potential of a system in an iterative process (Stern et al. 1997). The equilibrium constants for aqueous and solid species are calculated using the **Helgeson-Kirkham-Flowers** Equation of State (Stern et al. 1997), thermodynamic properties, or temperature and pressure dependent correlations of experimental data. Activity coefficients, partial molar densities, and other properties of aqueous species are calculated using the Bromley-Zemaitis or Pitzer excess property models (Stern et al. 1997).

ESP comes with several databanks covering most of the elements and compounds found or expected in Hanford Site tank wastes (Stern et al. 1996). These are supplemented with custom databanks that have been prepared specifically for simulating the processing of tank wastes.

Special databanks combined with associated chemistry models are used for almost all waste-related simulations.

A5 discussed in Section C.3.1, the compositions of the wastes in SSTs at the time of suspected leaks were developed using the HDW model (Agnew 1997). The HDW model provides supernatant compositions that were combined with leak volumes to project leak inventory estimates (Jones et al. 2000a). The tank waste supernatant compositions were then used as input to the ESP model with the goal of developing a better understanding of chemical speciation of the wastes at the time of suspected leaks. One of the weak points of the HDW model is its inability to reliably predict acid/base parameters such as pH or free hydroxide ion concentrations. However, the historical records (GE 1951; Harmon 1949; Barney 1976) clearly show that it was well known that the solution chemistry of REDOX HLW was dominated by the aluminum ion solubility and the aluminum solubility was controlled by the free hydroxide ion concentration. The selection of the free hydroxide concentration will dictate the thermodynamic modeling results for the REDOX HLW systems. Thus, much of the speciation modeling work discussed here focused on developing a better understanding of aluminum ion chemistry in the REDOX waste matrix. Such an understanding is potentially important in geochemical processes impacting tank waste movement in the subsurface.

The speciation calculation results reported in Jones et al. (2000a) use the tank waste compositions predicted by the HDW model at the times of the leaks for tanks S-104, SX-108, and SX-115. The previously reported results are supplemented here with additional modeling runs addressing the free hydroxide issue. These results are compared with results from Litchner et al. (2001). Corrections to errors in technetium-99 speciation estimates in Jones et al. (2000a) are also discussed briefly.

C.3.5.1 Aluminum Solubility in Reduction-Oxidation Wastes

One of the major characteristics of the REDOX HLW was the very high aluminum ion concentrations found in this waste stream (GE 1951). Aluminum ion solubility is closely coupled with the 'free' hydroxide ion concentration. An understanding of the aluminum ion chemistry in the REDOX HLW matrix is required in order to develop reasonable leak inventory estimates and address questions about waste-soil chemical reactions.

Aluminum nitrate was used as a 'salting out' agent in the REDOX liquid-liquid exchange columns to facilitate transfer of uranium and plutonium from the aqueous to organic phase. The high aluminum ion levels in the waste streams led to the development of carefully controlled processes for concentrating and neutralizing the HLW stream prior to being discharged to the SSTs (GE 1951). Considerable care was taken to avoid the precipitation of aluminum oxides during the concentration and neutralization processes because the formation of aluminum oxide solids in the waste stream led to problems in pumping the wastes. Since the long-term HLW management goals (Tomlinson 1963) required many waste transfers between tanks and processing facilities prior to final solidification, it is reasonable to assume that the free hydroxide concentration in the REDOX HLW streams would have been maintained at high enough levels to maintain essentially all of the aluminum ions in the solution phase (Barney 1975). However, there are inconsistencies in the historical records.

GE (1951) states that it was necessary to neutralize the HLW stream to a pH 13 to obtain a 'nearly clear liquid.' However, the manual also states that 25% to 30% excess caustic was required to reach that pH. Because the aluminum neutralization involved the reaction of 1 mole of aluminum with 4 moles of hydroxide to form sodium aluminate ($\text{NaAl}(\text{OH})_4$), a 25% to 30% excess caustic leads to 1 to 1.2 moles excess hydroxide being added per mole aluminum, during the neutralization process. Because the total aluminum concentration in the neutralized waste stream was approximately 1.2 moles, one would expect the free hydroxide concentration to be as high as 1.2 to 1.4 moles. However, some of the excess hydroxide would be neutralized by the excess nitric acid (1.2%), dichromate, iron, and uranium. Nevertheless, the excess hydroxide concentration in the waste stream going to the SSTs, would likely have been around 1 mole. The free hydroxide concentration would, of course, increase as the wastes were concentrated by self-evaporation in the tanks. REDOX boiling wastes were concentrated by a factor of approximately two until the beginning of 1963. After that point it appears the REDOX wastes were concentrated by a factor of closer to three in tanks SX-107, SX-108, and SX-109.

The arbitrary selection of 0.1 mole hydroxide for the preliminary speciation calculations reported in Jones et al. (2000a) was based on statements in GE (1951). However, the statement in GE (1951) that the waste was neutralized to pH 13 probably has little relationship to the hydrogen ion (or hydroxide ion) concentration in the waste. It is likely the pH 13 simply reflected an operations parameter that, in reality, only reflects the potential developed between a glass electrode and the reference electrode (likely to have been a calomel electrode). In a well-controlled laboratory environment, pH measurements can be converted to hydrogen ion activity (and concentration) in relatively simple systems. However, such a conversion is likely impossible in the REDOX waste matrix. Glass pH electrodes are, by design, highly selective for hydrogen ions but many also respond to sodium ion activity. Above pH 10, this 'sodium ion error' can become quite significant. There are also issues associated with the liquid junction potentials in the reference electrode. Finally, pH measurements are meaningful only if matrix-matched standards are available to calibrate the pH measurement system. Little is known about the pH monitoring systems or their operations in the REDOX Plant. Analysis of the REDOX process flowsheets leads to the conclusion that the hydroxide was at least an order of magnitude higher than the value used in Jones et al. (2000a).

The initial ESP speciation modeling of REDOX HLW, reported in Jones et al. (2000a), assumed a 0.1 mole free hydroxide concentration resulting in essentially all of the aluminum residing in the solid phase as aluminum hydroxide. Because of the uncertainty about the correct hydroxide concentration in the REDOX HLW, a sensitivity study was completed using the ESP model to assess the aluminum ion solubility in the waste matrix over a range of free hydroxide concentrations. The projected aluminum solubility data at 50 and 100 °C (122 and 212 °F) are shown in Figures C.10 and C.11. The aluminum solubility increases with increasing hydroxide reaching a maximum at 1 mole at 100 °C (212 °F) and 2 moles at 50 °C (122 °F), with essentially all of the aluminum in solution, as aluminum hydroxide. GE (1951) states that acidic REDOX HLW was cooled to slightly less than 50 °C (122 °F) prior to neutralization with 50% caustic. It is also stated that the wastes were neutralized to a 'near-clear' solution. Statements from GE (1951) coupled with aluminum solubility modeling results would suggest that the wastes contained in excess of 1 mol/L free hydroxide. Thus, it is almost certain that the HLW leaving the REDOX Plant would have contained in excess of 1 mol/L free hydroxide. The modeling results show the solubility to increase at higher temperatures therefore is likely that essentially all

aluminum ions remained in the solution phase during the boiling phase of the REDOX waste processing in the SX tank farm. This suggests that leaked tank wastes would have contained high levels of both aluminum ions and free hydroxide. This conclusion is supported by speciation calculations reported in Litchner (2001). The Litchner (2001) results are briefly described in Section C.3.5.2.

Figure C.10. Solubility of Aluminum in Tank SX-108 Waste at 100 °C (212 °F)

Figure C.11. Solubility of Aluminum in Tank SX-108 Waste at 50 °C (122 °F)

The second speciation modeling run evaluated the changes in solution composition as water was removed from the system. A REDOX HLW waste composition containing only major components was taken from GE (1951). Maximum aluminum ion solubility required 2.60 mol/L free hydroxide. The results shown in Tables C.8 and C.9 indicate the sodium nitrate is the first solid that precipitates from solution as water is removed. The aluminum ion solubility is not exceeded until approximately 45 % of the water is removed. These results are consistent with evaporator operations while removing water from high aluminum wastes (Barney 1975). Results are shown graphically in Figure C.12.

**Table C.8. REDOX High-Level Waste Components
During Volume Reduction (with Constant OH⁻)**

REDOX High-Level Waste (50 °C) – moles								Liq. Vol.
OH ⁻	Al(OH) ₄ ⁻	NaAlO ₂	NO ₃ ⁻	NaNO ₃ aq	Total NO ₃ aq	NaNO ₃	Liq. Dens.	
2.60	1.40	0.00	2.02	2.21	4.23	0.00	1.36	1.00
2.60	1.40	0.00	1.79	2.44	4.23	0.00	1.40	0.91
2.60	1.40	0.00	1.42	2.48	3.90	0.33	1.43	0.82
2.60	1.40	0.00	0.87	1.99	2.86	1.37	1.43	0.73
2.60	1.40	0.00	0.41	1.50	1.91	2.32	1.45	0.64
2.60	1.05	0.36	0.14	1.05	1.19	3.04	1.46	0.56
2.60	0.37	1.03	0.03	0.63	0.66	3.57	1.47	0.47
2.60	0.05	1.36	0.00	0.23	0.23	4.00	1.53	0.38

Table C.9. REDOX High-Level Waste Components Assuming Water Removal Only

OH-	moles/liter				Liq. Vol.	Solid Vol.	Solid Vol. Frac.
	Al(OH) ₄ -	NaAlO ₂	NO ₃ -	NaNO ₃ aq			
2.60	1.40	2.02	2.22	4.23	1.00	0.000	0.000
2.86	1.54	1.96	2.68	4.65	0.91	0.000	0.000
3.22	1.73	1.75	3.07	4.82	0.81	0.013	0.016
3.82	2.06	1.29	2.92	4.21	0.68	0.052	0.071
4.68	2.52	0.73	2.70	3.43	0.56	0.088	0.137
6.18	2.48	0.34	2.48	2.82	0.42	0.134	0.241
9.43	1.34	0.12	2.28	2.40	0.28	0.191	0.409
16.60	0.29	0.00	1.48	1.48	0.16	0.226	0.591

Figure C.12. REDOX Waste Chemistry During Water Removal

C.3.5.2 Los Alamos National Laboratory Speciation Results for Tank SX-108

The results reported in Litchner (2001) represent a far more detailed solution thermodynamic investigation than the results reported in Jones et al. (2000a). Litchner (2001) uses the Pitzer-based formulation for calculation activity coefficients. This approach is more consistent with contemporary geochemical modeling studies.

Any assessment of the soil-waste reactivity requires reasonable estimates of the chemical species present in the tank waste at the time of the leak. Litchner (2001) begins with estimated tank waste compositions reported in Jones et al. (2000a). The initial step in any speciation modeling exercise is the development a charge balance for the system. Jones et al. (2000a) fixes the hydroxide at 0.1 mole and allows the sodium ion to vary until the overall charge balance is reached, leading to sodium ion concentration near 12 moles. Litchner (2001) chooses to maintain the sodium ion concentration developed by the HDW model and allows hydroxide to be varied until a charge balance is reached. At equilibrium in tank SX-108 at 100°C (212 °F), Litchner (2001) predicts the hydroxide to be 5.1 moles and a pH of 14.1 with essentially all of the aluminum to be in solution as aluminum hydroxide. The Litchner (2001) speciation results are consistent with the conditions one would predict from process flowsheet data. Thus, these results are the preferred data set for geochemical modeling studies.

C.3.5.3 Technetium-99 Speciation

Technetium-99 has been identified as the major radioisotope of concern in recent risk evaluations at the Hanford Site. Based on theoretical calculations and Hanford Site reactor production records, it is believed that approximately 33,000 Ci of technetium-99 were produced at Hanford and processed through the various plutonium recovery processes (Kupfer et al. 1998). Currently, the fate of this technetium-99 is unclear. Although it is assumed in Kupfer et al. (1998) that for tank inventory estimates all of the technetium-99 produced in the plutonium-production reactors is currently stored in the 177 HLW tanks at the Hanford Site, it is widely understood that some fraction of the technetium-99 was shipped offsite as an impurity in the recovered uranium (Roberts et al. 1962), lost during intentional discharges of tank wastes to the soil column in the 1950s (Waite 1991; Corbin et al. 2001), and lost during various tank waste leak events. In addition to the uncertainty about the quantities and location of technetium-99 within the Hanford HLW tanks, there is considerable uncertainty about the chemical species of technetium-99 in individual tanks (Kovach et al. 1999). Thus, the preliminary speciation modeling results suggesting that major fractions of the technetium-99 could reside in the solid phase as potassium pertechnetate (KTcO_4) in highly concentrated REDOX HLW (Jones et al. 2000a) were of considerable interest.

Initial modeling runs indicated that the majority of technetium-99 in wastes in tank SX-108 was incorporated into the solid phase as potassium pertechnetate but in the more dilute tank SX-115 wastes the technetium-99 remained in the solution phase (Jones et al. 2000a). The implication was that technetium-99 was being 'salted out' of solution because of extremely high salt concentrations of these supernates. If the technetium-99 were predominately in the solid phase then the quantity of technetium-99 lost during a leak event would be reduced, as would the long-term risk. The possibility of technetium-99 being salted out of solution because of high ionic strengths could have had significant impacts on other tank waste related activities such as

waste retrieval and vitrification operations. Thus, the technetium-99 modeling results were critically reviewed.

A detailed review of the supporting information reported along with the speciation modeling results indicated that the potassium pertechnetate solubility was being driven by an unrealistically large activity coefficient term. Resolution of this issue was referred back to OLI Systems', the software vendor, for resolution. The vendor reported that a programming error was found in the code. Basically, the silicate ion activity was being summed with pertechnetate activity leading to errors in solubility estimates. After correcting this programming error, the model predicted that all technetium-99 remained in the solution phase in each SX farm tank waste composition. Although, to date, no technetium-99 analysis data have been found for REDOX HLW, the suggestion that technetium-99 tends to remain in the solution phase is consistent with experimental data for plutonium-uranium extraction HLW (Godfrey 1971).

¹ OLI Systems, Inc., Morris Plains, New Jersey.

C.4.0 GEOLOGY

This section presents a general discussion on the vadose zone geology in the vicinity of the SX tank farm.

C.4.1 REGIONAL GEOLOGIC SETTING

The Hanford Site is located within the Columbia Plateau of southeastern Washington State. This broad plain, situated between the Cascade Mountains to the west and the Rocky Mountains to the east, is underlain by a thick sequence of Miocene age tholeiitic basalt flows (the Columbia River Basalt Group). These basalt flows have been folded and faulted, creating broad structural and topographic basins, separated by asymmetric anticlinal ridges. Sediments of late Miocene, Pliocene, and Pleistocene age have accumulated **up** to 518 m (1,700 ft) thick in some of these basins. The Hanford Site lies within one of the larger of these basins, the Pasco Basin. This basin is partially bisected by the Umtanum-Gable Mountain anticline creating two subordinate synclinal basins. The largest of these is the Cold Creek syncline, which is further subdivided into two basins, the Wye Barricade depression and the Cold Creek depression. The Cold Creek depression underlies the principal WMAs of the Hanford Site, the 200 East and 200 West Areas.

The generalized stratigraphy beneath the Hanford Site consists of, in ascending order, the Columbia River Basalt Group, the Ringold Formation, the Plio-Pleistocene unit, and the Hanford formation (Figure C.13). Thin veneers of Holocene alluvium, colluvium, and/or eolian sediments discontinuously overlie these principal geologic units. More thorough descriptions of the regional geology, including the saturated zone of this area, are found in *Geology of the Separations Areas, Hanford Site, South-Central Washington* (Tallman et al. 1979), *Consultation Draft Site Characterization Plan* (DOE 1988); *200 West Groundwater Aggregate Area Management Study Report* (DOE-FU 1993); and “Geohydrologic Setting of the Hanford Site, South-Central Washington” (Lindsey et al. 1994).

C.4.2 GEOLOGY OF THE S AND SX TANK FARMS

The S and SX tank farms were constructed into the upper Hanford formation sediments underlying 200 West Area, along the north limb of the Cold Creek syncline. Stratigraphic units underlying or adjacent to the tank farms (in descending order) include backfill materials, lower Hanford formation sediments, the Plio-Pleistocene unit, and the Miocene- to Pliocene-age Ringold Formation.

Figure C.13. Generalized, Composite Stratigraphy for the Late Cenozoic Sediments Overlying the Columbia River Basalt Group on the Hanford Site

Sources: Johnson and Chou (1998); Johnson and Chou (1999).

The geology beneath the S and SX tank farms has been the subject of numerous reports. *Geology of the 241-SX Tank Farm* (Price and Fecht 1976a) presents an initial detailed interpretation of the geology. *Vadose Zone Characterization Project at the Hanford Tank Farms* (DOE 1996) presents an interpretation of the geology that is based primarily on groundwater monitoring wells constructed around the perimeter of the tank farm in the early 1990s. *Results of Phase I Groundwater Quality Assessment for Single-Shell Tank Waste Management Areas S-SX at the Hanford Site* (Johnson and Chou 1998) updates and refines the geologic interpretation. *Findings of the Extension of Borehole 41-09-39, 241-SX Tank Farm* (Myers et al. 1998) and *Geologic and Geochemical Data Collected from Vadose Zone Sediments from Borehole SX 41-09-39 in the S/SX Waste Management Area and Preliminary Interpretations* (Serne et al. 2001b) present detailed discussions on the geologic materials penetrated by the extension of borehole 41-09-39 (299-W23-234). *Subsurface Conditions Description for the S-SX Waste Management Area* (Johnson et al. 1999) further describes the geology and other subsurface contaminants. *Vadose Zone Geology of Boreholes 299-W22-50 and 299-W23-19 S-SX Waste Management Area Hanford Site, South-Central Washington* (Lindsey et al. 2000) provides additional interpretations on the geology, facilitated by the collection of near continuous split-spoon samples from boreholes 299-W22-50 and 299-W23-19. Geochemical analyses on vadose zone samples collected from borehole 299-W23-19, drilled through a contaminated zone immediately adjacent to SST SX-115, is the focus of this report (Figure C.14).

Borehole Data Package for Wells 299-W22-48, 299-W22-49, and 299-W22-50 at Single Shell Tank Waste Management Areas S-SX at the Hanford Site (Horton and Johnson 2000) contains a compilation of data packages on three groundwater monitoring wells (299-W22-48, 299-W22-49, and 299-W22-50) completed near the SX tank farm in 1999 and 2000. Most recently, *Subsurface Interpretation of the SX Tank Farm, Hanford Site, Washington Based on Gamma-Ray Logging* (Sobczyk 2000) presents a reinterpretation on the geology based on gross gamma-ray logs of 98 boreholes within the SX tank farm and the most recently published geology reports of the area (Johnson et al. 1999; Lindsey et al. 2000). Lastly, *Modeling Data Package for S-SX Field Investigation Report* (Khaleel et al. 2000) contains a detailed data package to support numerical simulation of the S and SX tank farms.

A hydrogeologic cross-section, constructed from a series of densely spaced boreholes beneath the SX tank farm is presented in Figure C.15. Some slight discrepancies may occur between the depths of the geologic contacts presented in this appendix and those presented in other documents, due to the various source of uncertainty in the geologic data sets and an individual geologist's interpretation. Johnson et al. (1999) describes the various sources of uncertainty for locating the stratigraphic contacts within a borehole as well as those uncertainties for drawing correlations between boreholes. That document identifies the principal sources of uncertainty as related to the drilling and sampling techniques, logging of the boreholes, and uncertainties in the geometric shape of the sedimentary units. Two different geostatistical techniques are used in Johnson et al. (1999) to evaluate the stratigraphy/depth uncertainty and finds that both techniques indicate that the stratigraphy beneath the S and SX tank farms is relatively consistent across the area. The optimal depths for stratigraphic correlations between different data sets were also found to be typically accurate to within 0.6 to 3 m (2 ft to 10 ft).

Figure C.14. SX Tank Farm and Vicinity Showing Location of Borehole 299-W23-19

Note: Location of cross-section A-A', represented in Figure C.15.

Figure C.15. Hydrogeologic Cross-Section of the Vadose Zone Beneath the SX Tank Farm

The stratigraphic terminology used in this report is summarized in Table C.10. The general stratigraphic interpretation presented here differs somewhat from that presented in Lindsey et al. (2000). The coarse (gravelly) materials found near the middle of the Hanford formation (correlative with Hanford H1 unit in Lindsey et al. [2000]) are interpreted to correlate across the tank farm and to represent a laterally continuous coarse unit distinct from the overlying and underlying finer sand units. Lindsey et al. (2000) suggests that these coarser materials are not continuous but rather represent thin, lenticular, discontinuous gravelly beds within stratified sand sheets of the Hanford formation. These differences are in interpretation only.

C.4.2.1 Columbia River Basalt Group

The Columbia River Basalt Group (composed of approximately 50 basalt flows) is more than 3,000 m (10,000 ft) thick and forms the bedrock beneath the Hanford Site. Sedimentary interbeds are sandwiched between the basalt flows, particularly in the uppermost Saddle Mountains Basalt. These interbeds, along with the porous basalt flow tops and flow bottoms, form confined aquifers that extend across the Pasco Basin (Reidel 1997).

The surface of the Columbia River Basalt Group lies at an elevation of approximately 26 m (85 ft) above mean sea level beneath the S and SX tank farms (a depth of approximately 175 m [575 ft] and dips gently to the southwest towards the axis of the Cold Creek syncline (Price and Fecht 1976a; DOE-RL 1993).

C.4.2.2 Ringold Formation

The Ringold Formation lies directly on top of the Columbia River Basalt Group and is approximately 125 m (410 ft) thick beneath the S and SX tank farms. The group locally consists of three principal stratigraphic units: (1) the fluvial gravels of unit A, (2) a fine-grained, paleosol-lacustrine sequence referred to as the lower mud unit, and (3) fluvial gravels of unit E (Figure C.13). The Ringold unit E gravels, depicted as Rwi(e) on Table C.10, are interpreted as equivalent to the Ringold Member of Wooded Island exposed along the White Bluffs, located along the eastern margin of the Hanford Site (Lindsey 1996). Ringold unit E grades upwards into fluvial sands of the upper Ringold unit (DOE-RL 1993), interpreted as an equivalent to the Ringold member of Taylor Flat (Rtf on Table C.10). Ringold unit E forms the main unconfined aquifer beneath the 200 West Area.

DOE-RL (1993) shows that the thickness of fluvial Ringold unit A is approximately 30 m (100 ft). Tallman et al. (1979) describes this unit as a silty-sandy gravel that is composed predominantly of gravel supported by a coarse-to-fine sand matrix with intercalated, lenticular beds of sand and silt.

The thickness of the lower mud unit is approximately 12 to 30 m (40 to 100 ft) (Tallman et al. 1979; DOE-RL 1993). This unit consists of predominantly mud (i.e., silt and clay); the lower portion contains well-developed argillic to calcic paleosol sequence (DOE 1988). The high clay content (up to 43% by weight) and the low hydraulic conductivity (perhaps as low as 10^{-12} ft/day) of this sequence acts to locally confine groundwater within unit A and form a base for the uppermost unconfined aquifer (Last et al. 1989).

**Table C.10. Stratigraphic Terminology Used in this Report
for the Vadose Zone Beneath the SX Tank Farm**

Stratigraphic Symbol"	Formation	Facies/Subunit	Description	Genesis
Holocene/Fill	NA	Backfill	Poorly sorted gravel to medium sands and silt derived from the Hanford formation (Price and Fecht 1976a).	Anthropogenic
H1a	Hanford formation	Unit H1b - gravelly sand	Top coarse sand and gravel sequence equivalent to the Johnson et al. (1999) 'Gravel Unit B.'	Cataclysmic flood deposits
		Unit H1a - slightly silty sand	Upper fine sand and silt sequence	
H1		Unit H1	Middle Coarse Sand and Gravel Sequence equivalent to 'Gravel Unit A' described by Johnson et al. (1999) and 'Hanford Unit A' described by Sobczak (2000).	
H2		Unit H2	Lower Fine Sand and Silt Sequence	
PP1z and/or H/PP1	Plio-Pleistocene unit	Upper	Very Fine Sand to Clayey Silt Sequence is interstratified silt to silty very fine sand and clay deposits at least partially correlative with the 'early Palouse soils' described by Tallman et al. (1979) and DOE (1988) and the 'unnamed Hanford formation [?]' or Plio-Pleistocene Deposits [?]' described by Lindsey et al. (2000), and the H/PP deposits in Wood et al. (2001).	Fluvial and/or eolian deposits (with some weakly developed paleosols)
PP1c		Lower	Carbonate-Rich Sequence. Weathered and naturally altered sandy silt to sandy gravel, moderately to strongly cemented with secondary pedogenic calcium carbonate.	Well-developed calcic paleosol or sequence of calcic soils.
Rtf	Ringold Formation	Member of Taylor Flat	Interstratified sand and silt deposits, equivalent to the Upper Ringold unit described by Tallman et al. (1979) and DOE (1988).	Fluvial and overbank-paleosol deposits
W1(e)		Member of Wooded Island, subunit E	Moderate to strongly cemented, well-rounded gravel and sand deposits, and interstratified finer-grained deposits.	Fluvial

*After Lindsey et al. (2000).

The thickness of unit E is estimated to be approximately 75 to 85 m (250 to 280 ft) (Tallman et al. 1979; DOE-RL 1993). This unit consists of well-rounded, clast-supported pebbles and small cobbles in a matrix of sand and mud. The amount of cementation is variable, with the lower portion of this unit described as moderately to well-indurated conglomerate (Tallman et al. 1979). However, zones of poorly indurated gravel and sand also occur within this zone. The upper part of the unit is generally poorly indurated. Borehole data in the immediate vicinity of the SX tank farm indicate that this upper portion is dominated by sandy gravel and muddy sandy gravel, with sand to muddy sand beds becoming more prevalent toward the top of the unit.

A relict erosional and weathered surface occurs at the top of the Ringold Formation beneath the SX tank farm (DOE 1988; Slate 1996; Slate 2000). The uppermost portion of this paleosurface is highly weathered and often cemented with secondary pedogenic calcium carbonate, referred to in this appendix as the carbonate-rich facies (subunit PPlc) of the Plio-Pleistocene unit (Table C.10). The northwest-southeast trending trough-shaped surface appears to conform to an ancestral Cold Creek channel and drainage system that developed following late Pliocene incision of the Ringold Formation, and prior to early Pleistocene cataclysmic flooding, during the period between approximately 2 to 3 million years ago (DOE 1988). The SX tank farm lies north of the ancestral Cold Creek paleochannel and the eroded Ringold paleosurface dips to the southwest beneath the SX tank farm. The attitude on this surface may have increased since late Pliocene-early Pleistocene time as a result of tectonic deformation associated with the Cold Creek syncline (Slate 1996; Slate 2000).

C.4.2.3 Plio-Pleistocene Unit

The Plio-Pleistocene unit lies unconformably on the tilted and truncated Ringold Formation that formed following incision and downcutting of the Ringold Formation by the ancestral Columbia River system, which began about 3.4 million years ago (DOE 1988). These deposits are inferred to have a late Pliocene to early Pleistocene age on the basis of stratigraphic position.

The Plio-Pleistocene unit includes all material overlying the Ringold Formation, including the weathered horizon at the top of the Ringold Formation, and beneath cataclysmic flood deposits of the Hanford formation (Lindsey et al. 1994). The Plio-Pleistocene unit includes the 'early Palouse soils' described in *An Eolian Deposit Beneath 200-West Area* (Brown 1960), Tallman et al. (1979), and DOE (1988); the 'Pre-Missoula Gravels' (or equivalent); the 'unnamed Hanford Formation [?] or Plio-Pleistocene Deposits [?]' described in Lindsey et al. (2000); and H/PP(?) deposits described in *Subsurface Conditions Description of the T-TX-TY Waste Management Area* (Wood et al. 2001).

Two distinct facies of the Plio-Pleistocene unit are recognized beneath the SX tank farm; these consist of an upper (PPlz) and lower (PPlc) subunit (Table C.10). The upper subunit PPlz is characterized by an abundance of silt, signified by the letter 'z,' and the lower subunit PPlc is characterized by an abundance of pedogenic calcium carbonate cement, signified by the letter 'c.' The combined total thickness of the Plio-Pleistocene unit is up to 13.1 m (43 ft) in the vicinity of the SX tank farm (Figure C.15). Subunit PPlz is relatively thick (up to 10.7 m [35 ft]), compared to the subunit PPlc, which measures only 1 to 4 m (4 to 13 ft) in thickness.

Subunit PPlc. The lower subunit PPlc represents a highly weathered paleosurface that developed atop the Ringold Formation (Brown 1959; Brown 1960), which represents a long period of surficial weathering in a semi-arid climate, similar to climatic conditions that exist today. Root traces and animal borrows, as well as other relict soil structures, point to a pedogenic origin for the calcium carbonate, although “Buried Carbonate Paleosols Developed in Pliocene-Pleistocene Deposits of the Pasco Basin, South-Central Washington” (Slate 1996) and *Nature and Variability of the Plio-Pleistocene Unit in the 200 West Area of the Hanford Site* (Slate 2000) also suggest the calcium carbonate could be associated with precipitation from paleo-groundwater levels. Calcium carbonate contents as high as 70 wt% have been reported within subunit PPlc elsewhere within the 200 West Area; however, the calcium carbonate content generally does not exceed 25 wt% in the vicinity of the SX tank farm. The calcium carbonate content from 3 randomly chosen boreholes within the SX tank farm did not exceed 10 wt%. Other names used for subunit PPlc, including ‘caliche’ and ‘calcrete’ are somewhat misleading because they imply a single, homogeneously cemented layer, which is not the case. Considerable internal variation exists, within subunit PPlc, often with multiple carbonate-cemented zones present (Bjornstad 1990; Slate 1996; Slate 2000; Wood et al. 2001).

The calcium carbonate overprint may occur on a variety of lithologies including silt, sand, felsic sand, and gravel as well as basaltic sand and gravel (Lindsey et al. 2000). In places, pedogenic alteration occurs directly on top of Ringold gravels (Rwi[e]) or sands (Rtf). In other places, the carbonate horizons occur within younger, pedogenically altered, fine-grained, eolian or sidestream-alluvial deposits overlying the Ringold Formation. The top of subunit PPlc is well defined by a coincident significant increase in calcium carbonate and decrease in mud content and sorting accompanied by a sudden and sustained decrease in total gamma activity (i.e., potassium-40) on borehole geophysical logs (DOE 1988; Last et al. 1989; Bjornstad 1990; Wood et al. 2001). In general, the top of subunit PPlc is easily identified by a sudden drop in total gamma activity that is usually, but not always, accompanied by a significant increase in calcium carbonate.

While the top subunit PPlc is relatively easy to recognize, considerable variation may exist internally within the subunit due to natural heterogeneity inherent of soils and soil processes that vary under different physical, chemical, and biological conditions (e.g., moisture, grain size, aspect, mineralogy, bioturbation, microbial activity). Added to this is the complicating factor that the land surface during Plio-Pleistocene time was undergoing many changes under the influence of local fluvial and eolian activity resulting in variable rates of aggradation, degradation, and soil development. Normally, only a single paleosol horizon is present within the lower Plio-Pleistocene unit within the SX tank farm, suggesting slow or negligible aggradation and/or subsequent erosion during paleosol development. This is in contrast to other areas to the west and south, which show up to five separate calcic horizons (Figure C. 16) separated by relatively noncalcareous, uncemented sand; silt; and even indigenous, basaltic sand and/or gravel (Slate 1996; Slate 2000; Wood et al. 2001). Multiple carbonate horizons within the subunit PPlc are indicative of several periods of calcic-soil development interrupted temporarily by periodic aggradational events (e.g., localized overbank flood, eolian accumulation, channel fill). The evolution of calcic paleosols and their morphogenetic development are discussed further in Slate (1996; 2000) and Wood et al. (2001).

Figure C.16. Lithofacies Distribution for the Lower Plio-Pleistocene Subunit PP1c

Modified from Slate (2000).

In WMA T-TX-TY, which is 1,800 m (5,900 ft) north of the SX tank farm, the top of subunit PPlc dips to the southwest at about 1" (Wood et al. 2001). At least some of the dip reflects the paleo-topography that existed during subaerial weathering of the eroded Ringold Formation surface. This is inferred based on the relief on top of subunit PPlc, which is almost double that of the underlying Ringold Formation lower mud unit. Therefore, it appears that during development of subunit PPlc there was a gentle dip to the land surface to the southwest toward the Cold Creek valley axis. Since Plio-Pleistocene time this surface has been steepened further by continued long-term downwarping along the north limb of the Cold Creek syncline (DOE 1988).

Another recognized facies of the Plio-Pleistocene unit is a coarse-grained side-stream-alluvial facies (Bjornstad 1984; DOE 1988; Slate 1996; Slate 2000), which is laterally equivalent to subunit PPlc to the south and west of SX tank farm. The side-stream alluvial facies (gravel facies in Figure C.16) fills and is restricted to the northwest-southeast trending, ancestral Cold Creek channel, located south and west of the 200 West Area. The eastern edge of this gravel facies occurs along the southwest boundary of 200 West Area near the SX tank farm (Figure C.16). North and east of the 200 West Area, the Plio-Pleistocene unit is generally not present, having been scoured away during either post-Ringold erosion and/or Pleistocene cataclysmic flooding.

C.4.2.3.1 Subunit PPlz. Unconformably overlying subunit PPlc is the upper subunit PPlz which consists of interstratified, uncemented fine sand, silt, and/or clay that only displays occasional, very weak soil development in the vicinity of the SX tank farm. Based on its fine-grained texture and relatively high natural-gamma activity on geophysical logs, this unit can be correlated across most of the 200 West Area (Wood et al. 2001). Subunit PPlz sediments appear to be predominantly fluvial-overbank type deposits intercalated with some eolian deposits (Lindsey et al. 2000; Slate 2000; Wood et al. 2001). Subunit PPlz is at least partially correlative with the 'early Palouse soils' described by previous reports (Brown 1960; Tallman et al. 1979; Bjornstad 1984; Last et al. 1989; Bjornstad 1990; and DOE 1988); the 'unnamed Hanford Formation [?]' or Plio-Pleistocene Deposits [?]' described in Lindsey et al. (2000); and the H/PP(?) unit described in Wood et al (2001).

The upper Plio-Pleistocene unit contains moderate amounts (up to a few weight percent) of calcium carbonate (Table C. 11), generally more than the overlying Hanford formation. As discussed previously, however, subunit PPlz may also locally have more calcium carbonate than the underlying subunit PPlc if samples from subunit PPlc come from noncalcic zones between paleosols within subunit PPlc.

Table C.11. Example of Granulometric and Calcium Carbonate Data from Drive-Barrel Samples of Subunit PPlz Encountered Beneath the SX Tank Farm

Borehole Depth	CaCO ₃ %	Gravel >2 mm	Sand					Mud <0.063 mm	Class
			Very Coarse 1-2 mm	Coarse 0.5-1.0 mm	Medium 0.25-0.5 mm	Fine 0.125-0.25 mm	Very Fine 0.063-0.125 mm		
299-W23-5 120 ft	2.6	0.0	1.8	1.9	4.8	12.3	31.1	48	mS
299-W23-5 125 ft	2.3	0.0	1.6	7.0	9.2	7.3	8.1	66.8	sM

The source of the calcium carbonate within the two subunits appears distinctly different. Within subunit PPlc, most of the calcium carbonate appears as stringers or in massive horizons, which formed in situ as a result of pedogenesis (Wood et al. 2001). Within subunit PPlz, on the other hand, the calcium carbonate is evenly disseminated and does not occur in discrete zones; therefore, it is interpreted to be detrital in origin (Wood et al. 2001). In fact, the bulk of the detrital, calcium carbonate mineral grains in subunit PPlz are probably derived from the disintegration and mechanical re-working and re-deposition of the underlying subunit PPlc.

The contact between subunits PPlz and PPlc is distinctive and easily identified. Subunit PPlz consists of relatively loose, stratified, non-pedogenically altered, well-sorted silt to very fine sand in contrast to poorly-sorted, weathered, and carbonate-cemented deposits of subunit PPlc. Also distinctive is a sudden increase in total gamma activity upward across the contact (DOE 1988; Last et al. 1989; Bjornstad 1990; Johnson et al. 1999). The upper contact of subunit PPlz with the overlying Hanford formation, on the other hand, often appears gradational, both texturally and structurally, and thus is often difficult to identify based on lithologic observations alone, especially in the vicinity of the SX tank farm. Because of this uncertainty, in the past subunit PPlz has been combined and queried with the lower Hanford formation in some recent reports (Lindsey et al. 2000; Wood et al. 2001). For the purposes of this study it was determined that the total gamma activity on borehole geophysical logs can effectively be used to identify the upper contact for the Plio-Pleistocene unit. Accordingly, a subtle decrease in total gamma activity appears to be associated with the top of subunit PPlz, probably as a result of a lower silt/clay content within the Hanford formation. Therefore, we recommend that this change in total-gamma activity and grain size be used to define the upper contact for subunit PPlz.

C.4.2.4 Hanford Formation

Pleistocene-age deposits of the Hanford formation overlie the Plio-Pleistocene unit and represent the dominant vadose zone materials directly beneath the SX tank farm. The Hanford formation is the informal name given to all deposits from Ice Age cataclysmic floods including any intercalated non-flood deposits.

The Hanford formation can generally be divided into three facies: (1) gravel-dominated, (2) sand-dominated, and (3) silt-dominated, also referred to as coarse-grained deposits, plane-laminated sand facies, and rhythmite facies, respectively (Baker et al. 1991).

The coarse-grained facies have also been referred to as the 'Pasco gravels,' and the rhythmite

facies as 'Touchet Beds.' The Hanford formation is thickest (up to 65 m [215 ft]) in the vicinity of the 200 Areas beneath Cold Creek bar (Figure C.17).

The gravel-dominated facies generally consists of poorly-sorted coarse-grained basaltic sand and granule to boulder gravel. These deposits occasionally display an open framework texture, massive bedding, plane to low-angle bedding, and large-scale fore-set bedding in outcrop. The gravel clasts (dominated by basalt) are usually subangular to subrounded. The gravel-dominated facies was deposited by high-energy floodwaters in or immediately adjacent to the main cataclysmic flood channel ways (Figure C.17).

The sand-dominated facies consists of fine- to coarse-grained sand and granule gravel displaying plane lamination and bedding and, less commonly, plane bedding and channel-fill sequences in outcrop. These sands may contain small pebbles and rip-up clasts in addition to pebble-gravel interbeds and silty interbeds less than 1 m (3 ft) thick. The silt content of these sands is variable, but where it is low a well-sorted and open framework texture is common. These sands typically are basaltic, commonly being referred to as black, gray, or 'salt-and-pepper' sands. The laminated sand facies was deposited at higher elevations where the floodwaters were starved of gravel, and/or adjacent to main flood channel ways during the waning stages of flooding (Figure C.17). This is a transitional facies between the gravel-dominated facies and the silt-dominated facies. The sand-dominated facies is the predominant facies of the Hanford formation beneath the SX tank farm.

The silt-dominated facies consists of rhythmically bedded, ripple-cross-laminated sand and silt, and fine- to coarse-grained sand grading upward to plane laminated silt. Individual rhythmites range from a few centimeters to several tens of centimeters thick (Myers and Price 1979; DOE 1988; Baker et al. 1991). These sediments were deposited under slack-water conditions and in back-flooded areas (DOE 1988), mostly around the margins of the basins (Figure C.17). The silt-dominated facies is the predominant facies of the Hanford formation south and west of the SX tank farm.

The Hanford formation beneath the SX tank farm is mostly represented by sand-dominated facies consisting of fine-grained sands intercalated with coarse sand and gravel and thinner lenses of silt. The basal portion of the Hanford formation is predominantly silty fine sand, described by DOE (1996) and Lindsey et al. (2000) as Hanford subunit H2 (Table C.10). A sandy gravel to coarse sand facies dominates the middle portion of the Hanford formation, which is then overlain by a slightly silty medium sand and finally by a slightly gravelly coarse sand. The middle coarse sand to gravel facies makes up the Hanford subunit H1 described in DOE (1996), Johnson et al. (1999), and Lindsey et al. (2000). The slightly silty medium sand and overlying slightly gravelly coarse sand is equivalent to the Hanford subunit H1a (Johnson et al. 1999; Lindsey et al. 2000).

Figure C.17. Digital Elevation Model Map of a Portion of the Pasco Basin Showing Routes and Facies Distributions for the Last Pleistocene Cataclysmic Floods

C.4.2.4.1 Subunit H2. The lower fine sand and silt sequence of the Hanford formation, H2 subunit, consists primarily of interstratified silty sands. This sequence generally thins from about 24.3 m (80 ft) east of the SX tank farm to approximately 10.7 m (35 ft) west of the tank farm (Figure C.15). Johnson and Chou (1998) suggests that this thinning may signify some scouring on top of the subunit, perhaps associated with a secondary flood channel similar to the north-south trending flood channel that bisects Cold Creek bar in Figure C.17. The grain-size within the Hanford H2 subunit appears to coarsen upward slightly (see Table C.12). Sobczyk (2000) and Johnson et al. (1999) report that the top of this unit generally dips about 6° to the southwest with some local relative highs and lows present throughout. Below subunit H2 are slightly finer-grained deposits of interstratified very fine sand; silt, and clay associated with the upper Plio-Pleistocene subunit PPlz. As mentioned previously, the base of the Hanford formation is indicated by a diagnostic increase in total-gamma activity on borehole geophysical logs.

C.4.2.4.2 Subunit H1. Subunit H2 is bounded above by subunit H1, and is a coarse unit dominated by gravel to gravelly sand and intercalated coarse sand (Table C.12) that appears to correlate beneath the SX tank farm (Figure C.15). This middle sequence—referred to as ‘Gravel Unit A’ in Johnson et al. (1999) and as ‘Hanford Unit A’ in Sobczyk (2000)—is equivalent to the H1 unit described in DOE (1996) and Lindsey et al. (2000). Subunit H1 ranges in thickness from 1 m (3 ft) to nearly 10 m (30 ft) beneath the SX tank farm. Sobczyk (2000) reports subunit H1 to be thickest beneath tank SX-102 (Figure C.14) where coarse-grained flood deposits backfilled an apparent channel eroded into the top of the underlying subunit H2.

Recent particle size results using dry sieving for 100 selected samples from 7 wells drilled in and around the tank farm reveal that this unit averages approximately 30% gravel, 66% sand, and only 4 % mud (see Appendix A). This is compared to the materials directly above and below it, that both average less than 1% gravel, nearly 90% sand, and 9% mud. Based on the modified Folk/Wentworth classification scheme, the classification of the average particle size for subunit H1 falls near the boundary between the sandy gravel and gravelly sand classes.

C.4.2.4.3 Subunit H1a. Above the middle coarse facies of the subunit H1 lies an upper fine sand to silty-sand sequence equivalent to subunit H1a described in Lindsey et al. (1994; 2000), and the ‘silty sand’ described in Sobczyk (2000). This sequence consists predominantly of interstratified slightly-silty medium to very fine sands (Table C.12) and ranges in thickness from 0 m (0 ft) where it was removed during excavation of the tank farm to about 9 to 12 m (30 to 40 ft) to the southwest (Figure C.15). Sobczyk (2000) reports that the top of this unit dips slightly (approximately 2°) to the southwest. Sobczyk (2000) also suggests that this unit may become coarser textured to the west.

C.4.2.4.4 Top Coarse Sand and Gravel Sequence (Hanford Subunit H1 - Coarse Unit B). A coarse-grained sand to gravelly sand unit (Table C.12) overlies the fine sand sequence of subunit H1a, and may be intercalated with some sandy gravel to the west. This unit is equivalent to Gravel Unit B (Johnson et al. 1999) and Hanford Unit B (Sobczyk 2000). It is the uppermost stratigraphic unit in the tank farm area, but is completely missing beneath the tank farm, where it was removed during construction. In surrounding boreholes, however, this unit ranges from a few meters in thickness to east to up 12 m (40 ft) to the west.

Table C.12. Data from Drive Barrel and Split-Spoon Samples of the Hanford Formation Beneath SX Tank Farm located in Figure C.14

Hanford Subunit	Borehole /Depth	CaCO ₃ %	Gravel >2 mm	Sand (mm)					Mud <0.06 3 mm	Class	Average Bulk Density from 299-W22-50*
				Very Coarse 1-2 mm	Coarse 0.5-1.0 mm	Medium 0.25-0.5 mm	Fine 0.125-0.25 mm	Very Fine 0.063-0.125 mm			
H1a	299-W23-72 55 ft	1.4	0.4	0.5	1	19.1	43.1	22.1	13.9	(m)S	1.95
	299-W23-92 80 ft	NA	2.1	3	12.1	20.4	31.2	19.8	11.4	(m)S	
H1	299-W23-72 70 ft	1.7	10.7	23.7	28.7	16.7	8.3	6.0	6.0	gS	2.27
	299-W23-92 90 ft	NA	16.3	16.9	27.9	18.5	8.1	5.7	6.6	gS	
	299-W23-108 85 ft	NA	41.8	24.5	14.5	7.1	3.9	3.3	5.0	sG	
H2	299-W23-72 100 ft	1.7	0.0	0.2	2.1	37.6	29.7	5.2	15.3	(m)S	2.05
	299-W23-92 110 ft	NA	0.8	1.0	9.4	40.0	22.2	14.6	12.0	(m)S	
	299-W23-92 120 ft	NA	2.8	2.2	1.7	9.6	33.5	34.9	15.4	(m)S	
	299-W23-108 110 ft	NA	1.8	0.1	1.8	13.2	26.6	30.9	15.7	mS	

Source: Horton and Johnson (2000).
NA = not analyzed.

C.4.2.5 Backfill

Geology of the 241-SX Tank Farm (Price and Fecht 1976a) describes the backfill surrounding the HLW tanks of the SX tank farm as consisting predominantly of poorly sorted cobbles, pebbles, and coarse to medium sands to silt derived from the Hanford formation. Lindsey et al. (2000) describes the backfill as relatively non-cohesive, friable, massive sand with variable amounts of silt and pebbles. A hardened zone at the base of the backfill, extending to a depth of approximately 18.6 m (61 ft) that was significantly harder and drier than the overlying materials was also observed.

Engineering drawings (H-237985, Sheets 1 and 2) show that the tank farm was excavated to create three terraces for construction of cascading tanks. This excavation extended to an elevation of 185.3 m (608 ft) on the west side and 185.9 m (610 ft) on the east side.

C.4.2.6 Clastic Dikes

Clastic dikes are vertical to near-vertically oriented sedimentary structures that cut across horizontal bedding planes. These dikes have been observed in all types and ages of geologic materials found beneath the Hanford Site including basalt; interbed sediments; the Ringold Formation; and the sands, mud, and gravels of the Hanford formation (Fecht et al. 1999). They are especially notable within the sand- and silt-dominated facies of the Hanford formation where they have been observed to be a few centimeters to more than a meter thick and extend to depths of 36 m (120 ft) or more. Clastic dikes may significantly impact contaminant transport through the vadose zone based on their differing orientation versus the traditional horizontal strata common in the Hanford formation.

Price and Fecht (1976a) states that clastic dikes were detected in the SX tank farm but that they could not be mapped. Clastic dikes (and/or polygonally patterned ground often associated with them) have also been observed at a number of locations surrounding the SX tank farm, including the SY tank farm to the north, the Environmental Restoration and Disposal Facility to the east, and throughout Cold Creek Valley to the south and west (including the former 216-S-16 pond). Tallman et al. (1979) indicates that identification of clastic dikes in this area was also based on examination of cable-tool drilling samples. Horton and Johnson (2000) reports that possible clastic dikes had been encountered by two or three recently installed RCRA groundwater monitoring wells (299-W22-48 and 299-W22-50). Lindsey et al. (2000) also notes a few structures suggestive of clay skins on clastic dikes in split-spoon samples from well 299-W22-50.

Figure C.18 illustrates one of the clastic dikes observed in walls of the excavation for the SY tank farm located approximately 300 m (1,000 ft) to the north of the SX tank farm (Price and Fecht 1976b).

Figure C.18. Clastic Diak in the SY Tank Farm Excavation

2001/DCL/SX41-09-39/002

Johnson et al. (1999) projects a plausible network of clastic dikes for the SX tank farm (Figure C.19) based on polygonally patterned ground mapped between Army Loop Road and State Highway 240 and scaled based on the best cell size estimate from *An Atlas of Clastic Injection Dikes of the Pasco Basin and Vicinity* (Fecht et al. 1999).

**Figure C.19. Projection of a Hypothetical Network of
Clastic Dikes onto Waste Management Area S-SX**

Source: Johnson et al. (1999).

C.5.0 MOISTURE CONTENT AND MATRIC POTENTIAL MEASUREMENTS

Moisture content and matric potential measurements are available for a number of boreholes in WMA S-SX (Myers 2000; Seme et al. 2001a, 2001b, 2001c). Many of the conclusions based on the measured matric potentials (Seme et al. 2001a, 2001b, 2001c) are presented in Section 3.2.1, in the context of recharge estimates for the tank farms. The primary purpose of this section is to present the measured data on moisture content and matric potential.

Moisture content measurements were made for sediments in the drywells surrounding the SX tank farm (Myers 2000). Matric potentials were measured for samples from two clean RCRA boreholes, 299-W22-48 and 299-W22-50 (Seme et al. 2001a), and also for the two contaminated boreholes: borehole 41-09-39 near tank SX-108 (Seme et al. 2001b) and borehole 299-W23-19 south of the SX tank farm (Seme et al. 2001c).

C.5.1 MOISTURE CONTENT FOR DRYWELL SEDIMENTS

The drywells at SX tank farm are generally within 1.5 to 3 m (5 to 10 ft) from the outside walls of the tanks. The drywells extend to various depths, typically between 22.8 and 30 m (75 and 100 ft). There are presently 98 drywells within the SX tank farm.

Within the backfill surrounding the SX tank farm, the measurements suggest that there is relatively consistent moisture content of 8 to 10% (volumetric), with a moderate increase in moisture at the base of the excavation (Figure C.20). The increased moisture content is possibly due to the increased compaction that took place during farm construction. In the undisturbed soils beneath the excavation, the presence of gravelly zones results in much lower moisture content, typically in the range of 4 to 6 vol%, with some drier zones. Thin zones of higher moisture content are evident below the tank farm excavation (Figure C.21). These thin zones are consistent with the presence of lenses or beds of silty fine sands noted in the Hanford formation. Deeper drywells exhibit a consistent increase in moisture content at a depth of about 38 m (125 ft) (Figure C.21). This depth corresponds to the approximate depth of the more massive fine, silty sands and sandy silts of the lower Hanford formation or Plio-Pleistocene unit.

Regions of greater than 12% moisture content (volumetric) were detected (Figure C.20). One of these zones was located east of tank SX-I 15. This location is defined by the high moisture content in a narrow zone in a single drywell at a depth about 21.3 m (70 ft). A second zone of high moisture content was identified north of tank SX-109 and appears as a halo starting at about 1.5 m (5 ft) bgs (Figure C.21). Research into the location of utilities serving the tank farm reveals that these readings are from a depth close to the terminus of an active water line. The presence of areas of noticeably wetter zones in vicinity of water distribution pipes points to the probability that these pipes may be significant sources of recharge.

In summary, the geologic environment of the SX tank farm plays a significant role in controlling the distribution of moisture with increasing depth. The distribution of moisture content, on the basis of drywell measurements, helps to identify areas where potential sources of recharge from water-line leaks may exist.

Figure C.20. Measured Moisture Contents for the Drywell Sediments Beneath SX Tank Farm

Source: Myers (2000).

**Figure C.21. Moisture Content Distribution for the
Drywell Sediments for Three Cross-Sections**

Source: Myers (2000).

C.5.2 MEASUREMENTS FOR BOREHOLES 299-W23-19, 299-W22-48, AND 299-W22-50

The gravimetric moisture content for sediments from borehole 299-W23-19 are shown in Figure C.22. The moisture content profile shows several high peaks within the Hanford formation coarse facies and the Hanford formation fine laminated sands. At 26.5 and 28.7 m (87 and 94 ft) bgs within the coarse unit, the higher moisture contents correspond to thin lenses of finer grained material. Within the fine unit there are wetter zones at 31 and 36 m (102 and 118 ft) bgs that do not seem to correlate with subtle changes in particle size. Within the Plio-Pleistocene unit fine grained facies there are 3 wet zones at 38.7, 43, and 45.7 m (127, 141, and 150 ft) bgs that correspond to thin zones of finer grained material. Wetter zones within the Ringold Formation may correspond to zones where water was added during hard tooling. Hard tooling was initiated at 49 m (161 ft) bgs and continued periodically down to 63.4 m (208 ft) bgs.

Figure C.22. Gravimetric Moisture Content Distribution for the Sediment Profile at Borehole 299-W23-19

Source: Serne et al. (2001c).

The moisture content profile in Figure C.22 is consistent with the measured data in Figure C.20 for near-surface sediments. The profile data in Figure C.22 are also consistent with those in Figure C.21 at about 21 m (70 ft) bgs and at about 37 m (120 ft) bgs. However, the observed high moisture contents at about 27 m (90 ft) bgs in Figure C.22 are not present in Figure C.21 near tank SX-115.

Matric potential measurements for samples from borehole 299-W23-19 and clean RCRA boreholes (299-W22-48 and 299-W22-50) are shown in Figure C.23. The soil suction (negative of matric potential) data are reported as head values in feet, consistent with reported depths bgs.

The higher the suction values, the less recharge is expected. On Figure C.23, an equilibrium line is also shown. Measured soil suction values to the left of the equilibrium line indicate that drainage (recharge) is occurring while values to the right of the line indicate that evaporation (drying or upward flow) conditions persist. As discussed in *Geologic and Geochemical Data Collected from Vadose Zone Sediments from Borehole 299-W23-19 [SX-115] in the S/SX Waste Management Area and Preliminary Interpretations* (Seme et al. 2001c), for RCRA boreholes 299-W22-48 and 299-W22-50 it appears that water from winter rains and snowmelt (or perhaps other sources) have penetrated the soil profile to depths of about 30 m (100 ft) bgs. However, below that depth the sediments from these two uncontaminated boreholes are significantly drier (i.e., to the right of the equilibrium line) compared to the sediments found in contaminated borehole 299-W23-19.

For borehole 299-W23-19 3 m ([10 ft] to the south-south-west of the side of tank SX-115), the suctions are low (sediments are relatively wet) throughout the profile and drainage is predicted to be the highest of any of the three boreholes. Note that borehole 299-W23-19 was drilled using air rotary and therefore no water was added during drilling. This is unlike the RCRA groundwater wells 299-W23-48 and 299-W22-50 boreholes, where water was added during hard tooling process of cable tool drilling. As discussed in Seme et al. (2001c), unit gradient conditions persist throughout the profile for borehole 299-W23-19 sediments but not for two clean boreholes outside the tank farm operations area. The accelerated drainage from water-line leaks south of tank SX-115 is believed to be the primary reason for the relatively low suction values (and higher recharge) for sediments from borehole 299-W23-19. Nonetheless, as discussed in Seme et al. (2001c), for this location an estimated recharge rate of between 50 to 100 mm/yr (2 to 4 in./yr) would be in line with the observed drainage rates from bare gravel surface soils at the Hanford Site (Gee et al. 1992).

C.5.3 MEASUREMENTS FOR BOREHOLE 41-09-39

Thirty sleeve sediment samples from the extension borehole for 41-09-39 near tank SX-108 were analyzed for moisture content and matric suction. The data, tabulated in Table C.13 and shown in Figure C.24, indicate that of the 30 samples 18 are at matric suctions lower (wetter) than the elevation of the sample above the water table (Seme et al. 2001b). As shown in Figure C.24, when the suction for a sample is less than the sample's elevation-above the water table, the sample is draining. As discussed in Serne et al. (2001b), in contrast to the other contaminated borehole 299-W23-19 matric suction values for samples from borehole 41-09-39 suggest a much drier moisture regime. Note that, because of extreme variability and uncertainty in some of the measurements, not all the data (Table C.13) are plotted in Figure C.24.

**Figure C.23. Soil Suction Profiles for 299-W22-48,
299-W22-50 and 299-W23-19 Borehole Samples**

Note: Dashed line is the equilibrium soil suction line. Drainage occurs only for values to left of the equilibrium line.

Source: Serne et al. (2001c).

**Table C.13. Water Content and Matric Suction Values
for Samples from Borehole 41-09-39**

Sample	Depth (ft bgs)	Water content (g/g)	Suction (m)	Sample	Depth (ft bgs)	Water Content (g/g)	Suction (m)
6F	141.9	0.11	3.93	37C	186.2	0.026	21.08
6E	142.4	0.096	5.38	38C	187.8	0.029	8.42
6D	143.3	0.218	12.74	38B	188.3	0.019	4.65
6C	144.1	0.26	3.3	39A	189.5	0.018	50.16
6B	144.7	0.229	5.03	40A	190.7	0.051	12.83
7C	146.4	0.112	26.81	47C	196.4	0.066	3.53
8C	148.3	0.074	14.99	50A	199.4	0.039	96.42
8B	149.9	0.097	9.6	56C	204.3	0.077	5.34
9A	152.8	0.139	6.04	56B	205.0	0.066	27.75
10C	153.4	0.136	24.86	56A	205.6	0.054	30.77
10B	153.9	0.147	2	58C	208.1	0.102	2.97
10A	154.5	0.196	4.8	58B	208.6	0.106	4.34
16D	162.3	0.133	0.25	59C	209.8	0.125	0.33
16C	162.8	0.135	2.21	59A	210.9	0.25	0.02
22B	172.0	0.052	5.54	64A	213.3	0.132	0.03

Source: Serne et al. (2001b).

Figure C.24. Matric Suction Profile for Samples from Borehole 41-09-39

Source: Serne et al. (2001b).

Serne et al. (2001b) presents three possibilities for the borehole 41-09-39 core samples having higher matric suction. The first is that much less drainage (recharge) is occurring at this borehole location ~~than~~ was observed at the other location at borehole 299-W23-19. The second is that the samples were disturbed enough during coring that the water content and possibly the density were altered enough to increase the matric suction values. The third is the possible drying effect due to heat load from the high-heat tank SX-108.

C.6.0 GEOCHEMISTRY

Numerous studies have been completed during the characterization of the WMA S-SX vadose zone that provide geochemistry information related to vadose zone contamination. Data provided by these studies are discussed in other sections and appendices of this WMA S-SX Field Investigation Report. Those investigations are briefly described here with appropriate references to other sections of this document for more detailed discussion.

The first and most extensive effort is the characterization of soil samples from the boreholes that have been drilled in support of this RCRA facility investigation. These include three characterization boreholes within WMA S-SX and two RCRA groundwater monitoring boreholes east of WMA S-SX. Soil samples were extensively analyzed for mineralogy and particle size distribution. Water and acid extracts were taken to measure water chemistry and radionuclide content. In a few samples, porewater was extracted without dilution from the soils and analyzed. These data are discussed in greater detail in Appendix B.

Several laboratory studies were completed to determine the chemical reactions controlling the mobility of cesium-137 and chromium. The results show that cesium-137 sorption is strongly influenced by the concentration of competing cations (primarily sodium and to a lesser extent potassium) for sorption sites and cesium-137 mobility has ranged from very high to very low. Chromium studies indicate that some retardation of chromium migration can occur by oxidation-reduction reactions. Cesium-137 and chromium studies are discussed in greater detail in Appendix D, Sections D.3.0 and D.4.0, respectively. Isotopic fission products were measured in borehole soils to gain insight on multiplicity of tank sources and their distribution in the soil column (Appendix D, Sections D.6.1, D.6.2, and D.6.3).

Finally, several modeling studies were completed to evaluate or incorporate geochemical parameters and their influence on contaminant migration. These included thermodynamic simulations to predict tank fluid chemistry (Appendix D, Section D.7.3) and flow and transport estimates of aqueous species migration (Appendix D, Section D.7.1 and D.7.4).

C.7.0 GROUNDWATER CONTAMINATION

Several groundwater monitoring wells around WMA S-SX have been contaminated during the last decade by constituents (primarily technetium-99, nitrate, and chromium) whose sources are postulated to be derived from one or more tank leaks (Johnson and Chou 1998; Johnson and Chou 1999b). Relatively high technetium-99 concentrations downgradient of WMA S-SX and occurrences of relatively high technetium-99/nitrate ratios similar to presumed tank liquid ratios have been the primary observations suggesting a link between observed groundwater contamination and tank leak contamination in the vadose zone. These data are also summarized in Johnson et al (1999). Since that report was issued, additional groundwater contamination data have been collected. This section summarizes some of the additional data provided in Johnson and Chou (2001). Where relevant to the discussion, data collected more recently than Johnson and Chou (2001) are also discussed in the main text.

The most recent groundwater contamination data from groundwater samples in several groundwater monitoring wells continue to support the hypothesis that the tank farm is the source of the contaminants. Sampling with depth was conducted at 4 new wells including well 299-W23-19 near tank SX-115, well 299-W22-48 east of S tank farm, well 299-W22-49 east of SX tank farm, and well 299-W22-50 at the southeast corner of the SX tank farm. Chemical species and radionuclide concentrations measured in these wells are listed in Tables C.14, C.15, and C.16. Technetium-99/nitrate and tritium/technetium-99 ratios are shown in Figures C.25 and C.26, respectively. Some outstanding features include the following.

- **Well 299-W23-19** – Shallow samples (0 to 6 cm and 1 m [0 to 5.5 in. and 3 ft]) were first taken in October 1999. Later samples in 2000 were taken at greater depth. There is relatively little variability with depth. Of note are the very high technetium-99 concentrations which continue to be high. Also, maximum technetium-99/nitrate ratios of 0.11 are observed, indicating a tank waste source.
- **Well 299-W22-48** – Moderate contaminant concentrations are observed. However, intermediate technetium-99/nitrate ratios of 0.039 occur, which may indicate a tank waste source.
- **Well 299-W22-49** – Moderate amounts of contaminants occur. The relatively high tritium/technetium-99 ratio indicates a non-tank farm source.
- **Well 299-W22-50** – Moderate contaminant concentrations occur. Maximum technetium-99/nitrate ratios of 0.11 are observed, indicating a tank waste source. The presence of increased nitrate and carbon tetrachloride at about 68 m (223 ft) indicates that an additional source, presumably the regional contamination plumes created by crib discharges, has contributed to contamination at this location.

In particular, technetium-99 groundwater concentrations measured in March 2001 have reached 81,500 pCi/L in well 299-W23-19.

Table C.14. Observed Contaminant Concentrations in Shallow and Extended Well 299-W23-19 Completions Near Tank SX-115

Constituent (unit)	Shallow Temporary Screen (1.5 m)		Permanent Screen (9.1 m)	
	October 1999 ^a		March 2000	June 2000
	Passive (Kabis, 0–6 cm)	Pumped ^b (1 m)	Pumped ^c (2 m)	Pumped ^c (2 m)
Technetium-99 (pCi/L) ^d	48,050	39,000	52,300	63,700
Chromium (µg/L) ^e	84	63	90	87
Nitrate, as NO ₃ (mg/L)	560	434	491	562
Tritium (pCi/L)	92,000	91,000	95,800	92,000
Specific Conductance (µS/cm)	1,199	1,003	968	1,237
Sulfate (mg/L)	18	16	18	17
Calcium (mg/L)	118	96	127	120
Magnesium (mg/L)	39	32	41	40
Sodium (mg/L)	34	34	42	43
Chloride (mg/L)	15	12	16	16

^aValues reported represent duplicate averages.

^b1.5 m (5 ft) screened interval with pump intake set at 1 m (3 ft) below the static water level.

^c9.1 m (30 ft) screened interval with pump intake set at 2 m (6 ft) below the static water level.

^dConcentration values of 81,500 pCi/L were measured in the March 2001 sample.

^eConcentration values of 138 µg/L were measured in the March 2001 sample.

Table C.15. Depth Distribution of Key Contaminants at SX Tank Farm Wells

Well	Sample Date	Depth (m)	Mode	Contaminants					
				⁹⁹ Tc (pCi/L)	NO ₃ (µg/L)	Cr. (µg/L)	³ H (pCi/L)	U (µg/L)	CCl ₄ (µg/L)
299-W22-48	10/26/99	0.6	DT/B	39.5	17,132	3.2U	122U	0.2	0.4
	03/30/00	2.3	S	720	18,593	7.1	249U	3.23	4
299-W22-49	11/04/99	0.5	DT	32.5	13,546	3.2U	22,000	0.82	0.6
	03/30/00	2.3	S	58.3	9,296	4.6U	22,000	3.27	6
	11/08/99	6.7	DT	2.96U	7,880	3.2U	18,900	0.92	1
299-W22-50	11/23/99	0.2	DT/B	4,240	57,991	3.0U	31,400	0.78	13
	04/03/00	2.3	S	3,230	30,102	10.4	24,200	4.29	11
	11/29/99	6.7	DT	812	12,838	3.0U	19,900	3.34	5.6
	12/14/99	11.9	DT	7.03U	2,125	3.0U	969	1.09	0.94
	12/15/99	28.7	DT	0U	1,151	3.0U	304	0.58	1.5
	12/17/99	53.0	DT	0U	3,187	3.0U	185U	0.79	5.6
	12/22/99	67.7	DT	0.577U	12,838	3.0U	0U	0.43	0.89
	01/12/00	99.4	DT	0U	4,869	3.0U	0U	30.90	0.23

*Depth is below water table.

DT = sampled during drilling using temporary pump/screen and packer assembly.

DT/B = bailed during drilling.

S = sample collected by pumping from 4.5 m (15 ft) screened interval.

U = analytical result is not detected.

Table C.16. Hydrochemical Parameters at SX Tank Farm Wells

Well	Hydrochemical Parameters								
	pH	Conductivity ($\mu\text{S}/\text{cm}$)	Alkalinity ($\mu\text{g}/\text{L}$)	SO_4 ($\mu\text{g}/\text{L}$)	Cl ($\mu\text{g}/\text{L}$)	Na ($\mu\text{g}/\text{L}$)	Ca ($\mu\text{g}/\text{L}$)	Mg ($\mu\text{g}/\text{L}$)	Na/Ca
299-W22-48	7.97	263	74,000	21,300	6,910	26,300	19,400	5,070	1.36
	8.59	295	---	19,200	5,900	27,000	22,200	6,910	1.22
299-W22-49	8.94	245	90,000	13,900	5,330	25,600	16,200	5,070	1.58
	9.09	240	---	11,900	2,800	23,300	17,600	5,960	1.32
	8.1	244	86,000	15,400	3,660	26,000	16,400	5,320	1.59
299-W22-50	---	---	100,000	14,200	4,800	28,200	23,200	7,300	1.22
	8.14	278	---	13,400	3,100	23,900	22,600	7,100	1.06
	8.1	235	101,000	12,500	2,500	20,400	17,800	6,020	1.15
	8.2*	228	106,000	14,400	3,100	11,600	26,300	9,250	0.44
	7.9*	242	114,000	14,400	4,400	12,700	28,700	10,200	0.44
	7.9*	307	126,000	16,100	15,200	14,300	33,400	12,400	0.43
	7.7*	323	115,000	19,300	10,000	15,500	33,000	12,500	0.47
	8.5*	234	96,000	18,900	5,800	16,600	20,200	8,010	0.82

*Laboratory result.

Figure C.25. Technetium-99/Nitrate Ratios for
Waste Management Area S-SX Network Wells

2001/DCL/S-SX/002

Given the well distribution showing relatively high technetium-99 concentrations, it appears that more than one tank waste source may be contributing to groundwater contamination. The largest technetium-99 concentrations (Table C.17) that have been recorded since 1997 occur at the southern end of the SX tank farm. This contamination is attributed to the tank SX-115 leak. A plausible plume distribution is shown in Figure C.27. The characteristics of this distribution are a 10-year plume narrowly constrained to the east-southeast whose source is in the vadose zone at or southwest of tank SX-115. The wells most clearly associated with this postulated plume are 299-W23-19, 299-W22-50, and 299-W22-46. All show identical technetium-99/nitrate ratios (Figure C.25) and show good fit with relative concentrations. There is some indication that this plume has rotated slightly over time to a more easterly direction because technetium-99/nitrate ratios and technetium-99 concentrations were high in well 299-W23-15. The technetium-99 plume has since moved away from this location (Figure C.27).

Other wells suggesting the occurrence of tank waste contaminants include 299-W23-1, 299-W22-48, and 299-W22-45 towards the north of WMA S-SX. The technetium-99/nitrate values in these wells are elevated relative to crib associated values west of WMA S-SX, but not as high as those at the south end of the SX tank farm. This suggests some vadose zone source under the S tank farm upgradient of these wells. Historical knowledge identifies only the tank S-104 leak as a source of relatively high technetium-99 content. Because the technetium-99 concentrations may still be rising in wells 299-W22-48, 299-W22-44, and 299-W22-45 (Figure C.28), future changes in contamination levels are uncertain here.

Figure C.27. Theoretical Groundwater Plume Dispersion Pattern from a Tank Leak Source in the SX Tank Farm Monitoring Efficiency Model

Figure C.28. Technetium-99 for Waste Management Area S-SX Network Wells

Table C.17. Maximum Contaminant Concentrations for Groundwater Samples Collected from Waste Management Area S-SX Network Wells (November 1997 to April 2000)

Analyte	MCL	W22-39	W22-44	W22-45	W22-46	W22-48	W22-49	W22-50	W23-1	W23-2
Chromium ^(a) (µg/L)	100	16.3	5 ^(b)	27.4 ^(b)	26	7.1	4.6U	10.4	29	6.1
⁹⁹ Tc (pCi/L)	900	120	56	2,080	5,330	720	58.3	4,240	2,890	75.6
Nitrate (as NO ₃) (µg/L)	45,000	16,822	37,628	47,367	49,580	18,593	13,546	57,991	50,023	11,952
Uranium (µg/L)	20	4.81	6.48	7.97	5.91	3.23	3.27	30.9	8.06	6.57
Gross alpha (pCi/L)	15	3.56	4.81	6.36	4.36	1.21	2.24	20.9	5.68	4.65
Gross beta (pCi/L)	50	37.5	20.7	768	1,836	223	22	1,420	1,090	29.3
Tritium (pCi/L)	20,000	27,100	238U	18,800	58,700	249U	22,000	31,400	1,010	12,700
⁹⁰ Sr (pCi/L)	8	0.261U	0.295U	1.4U	4.92U	0U	0U	1.03U	7.54	0.205U
¹³⁷ Cs (pCi/L)	200	1.82U	2.42U	2.78U	4.59U	0U	1.7U	0U	1.82U	0U
Iron ^(a) (µg/L)	300	118	146 ^(b)	65.9	122	54.9	85.8 ^(b)	95.5 ^(b)	59	39.5
Manganese ^(a) (µg/L)	50	7.7	8.1 ^(b)	3.8	4.3	306	244	167	7	11.8
Carbon tetrachloride (µg/L)	5	3.8	6.2	12	30	4	6	19	--	--
Fluoride (µg/L)	4,000	473	400	480	440	490	550	730	458	424
Aluminum ^(a) (µg/L)	50	51	58.3U	41.8U	45.7	41.8U	64.6	93.2	31.3U	20.6U
pH	[6.5, 8.5]	[7.93, 8.48]	[7.92, 8.25]	[8.07, 8.35]	[7.89, 8.33]	[7.97, 8.59]	[8.1, 9.09]	[8.1, 8.14]	[7.33, 8.19]	[8.11, 8.26]

Analyte	W23-4 ^c	W23-9 ^c	W23-13 ^c	W23-14 ^c	W23-15	W23-19 ^c	W23-234	Max ^d	Max/MCL
Chromium ^a (µg/L)	4.6U	8.5	33.9	12.5	8.1 ^(b)	89.8	7.5	89.8	0.9
⁹⁹ Tc (pCi/L)	21.1	408	10.6U	218	72.1	52,300	80.4	52,300	58.1
Nitrate (as NO ₃) (µg/L)	4,869	165,562	7,698	134,575	14,697	562,204	19,080	562,204	12.5
Uranium (µg/L)	24.4	25.8	16.5	18	14.6	17.6	3.4	30.9	1.5
Gross alpha (pCi/L)	14.5	17.3	11.7	9.82	10.8	21.9	--	21.9	NA
Gross beta (pCi/L)	15	56.6	11.4	19.7	27.8	23,000	--	23,000	NA
Tritium (pCi/L)	1,540	502,000	215U	382,000	22,200	95,800	138,000	502,000	25.1
⁹⁰ Sr (pCi/L)	0.222U	0.481U	0.189U	0.425U	0.36U	9.63U	0.2U	7.54	0.94
¹³⁷ Cs (pCi/L)	3.96U	0U	1.33U	1.71U	2.31U	1.63U	1.3U	Not detected	NA
Iron ^a (µg/L)	81.5	83.3	154	110	938	46	48.2	938	3.1
Manganese ^a (µg/L)	2.4	30.3	10.2	12.7	20.1	203	5.7	306	6.1
Carbon tetrachloride (µg/L)	100	2	11	0.51	140	22	--	140	28
Fluoride (µg/L)	340	319	390	350	490	340	497	730	0.2
Aluminum ^a (µg/L)	41.8U	41.8U	41.8U	33.5U	83.2	41.8U	33.5U	93.2	1.9
pH	[8.0, 8.09]	[7.72, 8.1]	[7.72, 8.58]	[7.78, 8.52]	[7.74, 8.12]	8.05	8.54	[7.33, 9.09]	NA

Note: All well numbers prefixed by 299-. U denotes analytical result is not detected. Bold indicates well with maximum.

^aFiltered sample results.

^bOutliers removed.

^cUpgradient wells.

^dMaximum across all network wells.

^eSubsequent groundwater sample analyses show increases in chromium and technetium-99 concentrations (138 µg/L and 81,500 pCi/L, respectively) as of March 2001.

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APPENDIX D

DIGEST OF S&T PROGRAM EVALUATIONS

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D.1.0 OVERVIEW AND SUMMARY

The Hanford Science and Technology Program (S&T Program) was initiated in 1998 with the overall goal of coordinating and performing mission-oriented scientific research in support of environmental management decision making for the 200 Areas at Hanford. The scope of the S&T Program, as well as the major site milestones that it supports, has been described in the Science and Technology Roadmap for the Hanford vadose zone (DOE 2000). The S&T Program consists of focused, site-specific investigations funded by DOE-Richland Operations through the Groundwater Vadose Zone Integration Project, and Environmental Management Science Program (EMSP) projects funded in the FY 1999 vadose zone call.

The Integration Project has used the process of roadmapping, where problem holders (such as the U.S. Department of Energy (DOE), Tribal Nations, regulators, stakeholders, and remediation contractors) come together with problem solvers (such as scientists and engineers from universities and the DOE national laboratories) to define the problems and establish a path to solution. The scope and outcomes of S&T Program activities, linkages of the outcomes to the Integration Project or other Hanford Site projects, and the schedule, budget, and priorities for these activities are documented in the S&T Program roadmap, which was issued and revised once (DOE 1999; DOE 2000).

This particular appendix contains research performed by three elements of the Hanford S&T Program: Representative Sites Research, Reactive Transport Modeling, and Vadose Zone Field Experiments. This scientific input by the S&T Program to the Waste Management Area (WMA) S-SX Field Investigation Report represents a specific milestone in the S&T Program roadmap. The research addressed a number of key scientific issues associated with tank waste source terms; the chemical speciation of Reduction-Oxidation (REDOX) tank wastes, water and contaminant fluxes through the vadose zone at WMA S-SX, and the geochemical behavior of ^{137}Cs , Cr, and ^{99}Tc . These issues were studied through experiments with uncontaminated (borehole B8812) and contaminated subsurface sediments (299-W23-19, 41-09-39, tank SX-108) from the S and SX tank farms (Representative Sites); modeling studies of heat, water, and contaminant flux through the S-SX vadose zone (Reactive Transport Modeling); and field injection experiments at the Vadose Zone Transport Studies Site.

This appendix summarizes key results of the S&T Program research that have important implications to (1) conceptual models of water and waste migration in the vadose zone, and (2) future migration and in-ground chemical behavior as it may influence future discharges to groundwater, need for corrective actions, and leak-loss limits for tank waste sluicing. In the interest of brevity, many details and the supporting experimental, theoretical, and computational information have not been included in the scientific summaries that follow. Readers desiring full disclosure of methods and results are best directed to the peer-reviewed publications that are resulting from this work.

D.1.1 KEY FINDINGS

The most important findings of the S&T Program investigations and their implications are summarized below. Details of these findings and other equally important conclusions may be found in the individual technical sections.

- (1) Laboratory studies Environmental Management Science Program of the interaction of highly basic REDOX waste simulants with S-SX sediments have shown that significant mineral alteration and precipitation (e.g., of zeolites) occurs as a result of waste-sediment reaction. As a result, it was speculated that a large/deep mineral alteration aureole would surround the leaked tanks, which would impact contaminant behavior. Field observations, in contrast, showed that this alteration zone was much reduced in depth (e.g., only 67.27 ft, sample 3A in SX-108 core), although clearly apparent through microscopic analysis of the sediment grains. Most contaminants were observed at depths deeper than the mineral transformation zone, suggesting that such reactions were of minimal consequence to contaminant retardation and need not be considered in terms of future mobility issues in the S and SX tank farms. Mineral and surface analyses of sample 5A from the SX-108 core, which contained low contaminant levels, showed that surfaces were pristine, indicating that reactive tank wastes did not migrate through this sediment. A heterogeneous vertical migration pattern is inferred.
- (2) The ^{137}Cs distribution coefficient is not constant over the range of sodium, potassium, calcium, and cesium concentrations found in the tank farm inventory and in the vadose zone porewater. Vadose zone processes, such as dilution from infiltrating rainwater (or water leaking from pipes), or concentration from boiling waste, will dramatically alter the ^{137}Cs - K_d over time and space. The multi site cation exchange model developed by EMSP researchers captures many of the chemical effects responsible for the dependence of ^{137}Cs - K_d on competing cation and Cs concentrations, and is a significant improvement over a constant K_d to model ^{137}Cs transport from tank leaks and to predict its future in-ground behavior.
- (3) The deep penetration of ^{137}Cs may be explained as resulting from the competitive ion exchange effects of high Na and K present in REDOX wastes and possibly by the bypassing of exchange sites in immobile regions during unsaturated flow. New, charge-balanced calculations performed to estimate the total composition and speciation of leaked wastes from tanks SX-108 and SX-109 suggest that the Na^+ concentration was higher than previously thought, possibly approaching 19.6 and 15.2 mol/L for tanks SX-108 and SX-109, respectively. The chemical effects of these high electrolyte concentrations, alone, yielded predicted values of ^{137}Cs retardation (2 to 3) that were remarkably close to observed values below tank SX-108 (2.5 to 3), although these conclusions were based on one-dimensional flow and transport simulations that may not be applicable to the complex flow system developed around the boiling tank SX-108. The current in-ground Cs is in approximate ion exchange equilibrium with its surroundings.
- (4) Approximately 50% of the large in-ground adsorbed $^{133,135,137}\text{Cs}$ pool in WMA S-SX sediments is labile and exchangeable with the aqueous phase. The fission-derived Cs is

sorbed to micas and smectites, with no other phase associations observed. Significant desorption and transport, as could feasibly occur if fluids were released by waste sluicing, however, is not expected unless aqueous concentrations of Na and K exceed those present in the original, leaked REDOX wastes. Such conditions are considered highly unlikely.

- (5) X-ray absorption (XAS) measurements by EMSP investigators showed that Cr existed in two valence states (III, VI) in contaminated sediments from both 41-09-39 and tank SX-108. Cr(III), which is relatively immobile, is believed to result from the heterogeneous reduction of CrO_4^{2-} in the REDOX tank wastes by Fe(II) contained in sediment minerals (biotite, ilmenite) to insoluble hydroxide precipitates. Laboratory studies indicated that this reaction was base (e.g., OK) facilitated and may no longer be operative. The water extractable Cr was consistent with that present as Cr(VI) (CrO_4^{2-}). Approximately 30 to 60% of the Cr present in tank waste was immobilized in sediment as Cr(III) precipitate, with the remainder present as water-soluble CrO_4^{2-} . Fission-derived Mo (presumably as MoO_4^{2-}) appeared to follow similar reductive processes to Cr, while $^{79/82}\text{Se}$ (SeO_4^{2-}) and $^{99}\text{TcO}_4^-$ were freely mobile. These mass balance issues must be considered when using Cr(VI) concentrations in groundwater as indications of tank waste contribution.
- (6) The isotopic ratios of trace anionic fission products ($^{127}\text{I}/^{129}\text{I}$; $^{95}\text{Mo}/^{98}\text{Mo}$) in water extracts varied significantly between regions of the SX-108 core showing peak concentrations in mobile constituents (e.g., NO_3 , Cr, ^{99}Tc). These isotopic ratios provide a means for tracing waste sources and leak events if the "fill history" of the tank and its time variant isotopic signature is sufficiently documented. The trace isotope analyses of waters extracted from tank SX-108 indicate that wastes of different isotopic composition were discharged to the vadose zone from tank SX-108. The results may imply the time-separated intrusion of leaked waste of different composition into the subsurface, most likely associated with the two known fillings of the tank in 1959 and 1963. Further evaluations of the tank fill history and the isotopics of the REDOX and other comingled wastes (Al-cladding waste and condensate) are needed to formulate a consensus conclusion on the implications of the measurements.
- (7) An assessment of the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios in the B8812 core indicated an average water infiltration flux of 30 ± 20 mm/yr to the vadose zone over the past 100 to 1000 years. In contrast, infiltration estimates for the S and SX tank farms based on a method that uses winter precipitation and surface soil texture data, calibrated by 20 years of Hanford lysimeter data, place the average value at 56 mm/yr with a range of 20 to more than 150 mm/yr, depending on climatic conditions. Regardless of precise value, these results suggest that natural infiltration and drainage is significant for moving mobile species (e.g., NO_3 , Cr, ^{99}Tc , $^{127/129}\text{I}$, $^{79/82}\text{Se}$) toward groundwater over time periods of decades to hundreds of years. The estimated vadose transit time for meteoric waters in the S and SX tank farms range from 60 to 500 years depending on assumptions and model.
- (8) A microbiological enumeration was performed on contaminated SX-108 sediments to determine if microorganisms were present that could influence the long-term fate of the

in-ground contaminants. Culturable microorganism populations of chemoheterotrophic bacteria were found in samples 1a, 4a, 7a, 9a 12a, 16a, and 17a. Some of the organisms found can use nitrate as an electron acceptor in the absence of O_2 and reduce contaminant metals/radionuclides [Cr(VI), Tc(VII)] to insoluble species in presence of a sufficient energy source. Radiation-resistant-bacteria, closely related to *Deinococcus rudiocurans*, was isolated from two core samples containing high levels of ^{137}Cs . This is the first time that *D. rudiocurans* has been isolated from a radionuclide-contaminated environment.

- (9) Significant horizontal movement of water along the top of the Plio-Pleistocene caliche was implied by moisture content, isotopic measurements, and solute displacement from B8812 core materials. While the source of these waters and the entrained contaminants has not been identified, the observations affirm that water perching and lateral transport may occur on the Plio-Pleistocene contact beneath the S and SX tank farms.
- (10) Field injection experiments at the Vadose Zone Test Facility performed by a team of EMSP and S&T Program investigators near PUREX in 200 East indicated that subtle changes in sediment texture can induce the lateral spreading of draining vadose zone waters and their entrained contaminants. In particular, the layering anisotropy of fine over coarse sediments can produce significant lateral spreading of a plume that generally retards and reduces the downward migration of solutes. These findings provide a physical model for various observations in the S and SX tank farms, including (1) elevated water contents found at depth in 41-09-39, tank SX-108, and 299 W23-19 associated with layer sequences of finer-textured sediments, and (2) heterogeneous localization of ^{137}Cs in specific lithologies and apparent horizontal migration as inferred by downhole gamma spectral logging.
- (11) Nonisothermal model simulations indicate that the thermal load from the boiling waste tanks altered water seepage patterns and caused large-scale redistributions in moisture. During periods of **high** heat load in the 1950s and 1960s, fluid and heat flow near the tank was dominated by vapor-liquid counterflow. Such counterflow concentrated dissolved solids near the heat source as precipitates. The heat load caused formation dry-out beneath the tank that was also accompanied by near-tank solute precipitation. Salt precipitates may have been remobilized at later times when tank temperatures declined and previously dried out regions began rewetting. Such effects may complicate the interpretation of solute distribution patterns in the SX-108 core. It is expected that solute distribution profiles in the infiltration shadow beneath the center of the tank will be different than in the region of enhanced seepage fluxes around the tank perimeter because of dilution and solubilization effects of dry-out induced salt precipitates.
- (12) When compared with simulations done under isothermal conditions, nonisothermal model calculations indicate slightly faster transport through the vadose zone to the water table even when transport begins at present. Lower saturations induced by the tank heat result in shorter travel times and more lateral migration toward the compliance boundary. This effect may increase when the thermal impact of tank leaks (e.g., ^{137}Cs decay) is also considered. The model simulations (isothermal,

nonisothermal), however, assumed a constant recharge of 100mm/yr at the soil surface and did not allow for evaporation. Residual heat from the tanks may enhance surface evaporation and reduce recharge, an effect that would slow solute migration toward groundwater. Additional nonisothermal modeling will address such issues.

- (13) The vertical distribution of anionic and cationic solutes in borehole 299-W23-19 were well matched with a three-dimensional transport model that included multicomponent cation exchange as the primary chemical retardation mechanism. The model was parameterized with laboratory measurements of cation exchange capacity and ion selectivity and assumed that all cation exchange sites in the sediment were accessible to the tank solutes. While the 3D simulations used laboratory CECs and selectivity coefficients without calibration, the tank fluids leaking into the vadose zone had to be diluted from the charge-balanced estimates. In addition, some questions remain whether the 3D flow model, despite having used the accepted hydrostratigraphy of the Hanford formation, captured the full effects of the heterogeneities present. However, the good agreement between model and data suggested that sediment exchange sites were not being bypassed in the transport event. Accordingly, there is presently no evidence that the solute distributions were influenced by phenomena associated with expedited migration such as fast flow pathways or transport-limited sorption in immobile water zones. By analogy, it appears that the enhanced migration of ^{137}Cs noted beneath tank SX-108 was a result of its different chemical environment (e.g., high Na), although the higher temperatures associated with tank SX-108 may have produced a substantially different flow regime.

D.1.2 OBJECTIVE OF THE INTEGRATION PROJECT AND THE S&T PROGRAM

The Integration Project was established by DOE to ensure protection of the Columbia River environment, including river-dependent life and users of river resources. The Integration Project is accountable for the integrated management of vadose zone, groundwater, and Columbia River activities at the Hanford Site. This role involves five elements designed to:

- integrate characterization and assessment work affecting long-term risk assessments (Integration)
- assess the potential long-term effects of Hanford contaminants (System Assessment Capability [SAC])
- enhance the role of science and technology in cleanup decisions (S&T Program)
- ensure productive involvement by parties interested in influencing Hanford's cleanup (Public Involvement)
- ensure independent technical reviews and management oversight of the Integration Project (Technical Review).

These are described in Volume I of the *Project Summary Description* document.

The objective of the S&T Program is to provide new knowledge, data, tools, and the understanding needed to enable the Integration Project's mission. The S&T Program is focused on resolving key technical issues that help inform and influence decisions on remediation and closure of tank farms and contaminated soil sites, in partnership with both the SAC and core projects (those projects that are influenced by the Integration Project).

D.1.3 APPROACH

For each of the technical elements contributing to the S&T evaluation of WMA S-SX, a approach was developed.

D.1.3.1 Tank SX-108 Implementation Plan

The ORP Tank ~~Farm~~ Vadose Zone Project developed a plan for characterizing samples from the slant borehole at tank SX-108. This characterization was performed to determine the general state of conditions (chemical/radiological and physical) beneath tank SX-108. The results of the tank SX-108 analyses were integrated with those from the uncontaminated boreholes (e.g., B8812 and B8814), the decommissioning of 41-09-39, and the SX-115 borehole. Together with the contributions from the S&T Program effort, a greatly improved conceptual model of subsurface tank waste migration at WMA S-SX was developed.

The scientific studies of the uncontaminated and contaminated samples complemented the ORP ~~Tank Farm~~ Vadose Zone Project characterization with definition of the physical, chemical, and mineralogic association of contaminants; their chemical status and environment; their degree of immobilization or reversibility; their potential for future mobilization; and other such issues. The planning of the wraparound science was, in part, accomplished through EMSP vadose zone workshops held at Pacific Northwest National Laboratory in November 1999 and November 2000. These workshops brought together the principal investigators of EMSP projects and Hanford Site personnel, including staff of the ORP.

To prepare for the characterization activity at tank SX-108, the ORP developed inventory estimates for tank waste in tank SX-108 at the time of the leak, and a leak history scenario. The inventory estimate allowed identification of primary contaminants of concern (COCs; ^{137}Cs , ^{99}Tc , CrO_4^{2-}) and their potential concentration ranges, and other constituents (e.g., Na , NO_3^{2-} , OR , $\text{Al}(\text{OH})_4^-$) that will impact contaminant mobility. In addition, the best estimate of tank SX-108 composition at the time of the leak(s) was substantially greater (by at least a factor of five) than that estimated for tank SX-115. The concentration range is significant in that the advanced scientific equipment that may be used to investigate the chemical environment and reactivity of contaminants (e.g., optical and X-ray absorption spectroscopy and microscopy) requires certain minimal concentrations for effective application.

The plan for the SX-108 slant borehole was to retrieve samples immediately beneath the leaked tank, and from the distal region of the vadose zone plume using a 2-inch diameter, 1-foot long shielded split spoon. Precautions were taken to seal the retrieved core to prevent drainage and oxygenation after collection as soon as radiation protection and environment, safety, and health procedures allowed. Approximately 500 g of each sample were made available for S&T Program research. Poor core recovery may further limit sample availability. The high potential radioactivity of the core materials resulting from sorbed ^{137}Cs mandates that extreme care be taken in distributing and handling the core materials and that all appropriate environment, safety, and health and radiation protection procedures be followed at Pacific Northwest National Laboratory and receiving institutions. A separate environment, safety, and health plan for the distribution of these samples was developed and implemented. All samples were distributed to investigators, retrieved, and dispositioned without incident.

D.1.3.2 Transport Modeling

The Transport Modeling element performed analyses to identify appropriate detail in process models for Hanford Site assessments and provide technical defensibility for their use in predicting long-term contaminant behavior. The S&T Program modeling is based on historical data for the Hanford Site as well as the results of recent characterization efforts and scientific investigations. The data used by the modeling team have been or are being developed by other entities (e.g., other national laboratories through the S&T Program or EMSP, Site contractors, etc.) for a variety of purposes. Most of these data were previously not examined in a comprehensive modeling framework for consistency. An important role for the S&T Program modeling, therefore, was to identify inconsistencies between observations and process-level understanding and identify areas that merit additional investigation.

The S&T Program modeling addressing the nonisothermal multiphase fluid flow modeling was performed in two-dimensional cross sections, with the TOUGH2 (Pruess et al. 1999) and STOMP (White and Oostrom 2000a, b) codes. In each effort, two-dimensional cross sections were used to represent the vadose zone beneath WMA S-SX. The STOMP simulations used the data package (Khaleel et al. 2000) developed for the Tank Farm Vadose Zone Project projections of solute transport under isothermal conditions. The S&T Program modeling was performed to test the isothermal assumption by performing nonisothermal multiphase simulations.

Reactive transport modeling was performed on the tank SX-115 leak by coupling the reactive transport code CRUNCH (Steefel 2001) with the multiphase flow and heat transport code NUFT (Nitao 1998). In addition to the flow and transport parameters documented in Khaleel et al. (2000), the reactive transport simulations used ion exchange parameters extracted from batch and transport experiments performed as part of the WMA S-SX S&T Program investigations.

D.1.3.3 Vadose Zone Transport Field Studies

The detailed test plan (Ward and Gee 2000) outlines the overall scope of the field experiments. The first 2 years of field experiments were performed at a test location in the 200 East area previously known as the Sisson and Lu site (299-E24-111) where a previous injection experiment was performed and extensive characterization data already were compiled. Data were collected in several phases: (1) characterization of background conditions at the site, and (2) process characterization that occurred during and after the field injection experiment. Background moisture conditions at the site were determined, and a series of fluid injections, designed to simulate a leak from a high-level waste tank, was performed over a 3-month period. The field test involved water and tracers to simulate dilute tank wastes. A second injection experiment is being conducted during FY 2001 involving dense saline fluids with tracers to simulate high-salt wastes. Nine monitoring technologies were used, including neutron logging, electrical resistance tomography, cross-borehole radar and seismic, high-resolution resistivity, electromagnetic imaging, advanced tensiometry, and isotopic tracers. Water contents, obtained by neutron probe logging and coring, provided baseline measurements for comparison of other geophysical measurements.

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D.2.0 S-SX SITE MINERALOGY

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D.2.1 INTRODUCTION

The sediment mineralogy Beneath the SX tank farm directly impacted the mobility and fate of caustic wastes that leaked from compromised tanks. The impacted sediments were fine sand with potentially reactive mineral components (Bjomstad et al. 1987), including the micaceous minerals muscovite and biotite, laumontite, smectite and kaolinite clays, and a lithic component that was dominated by basalt clasts. The latter included abundant volcanic glass, which might preferentially react with alkaline wastes. The alkaline waste reacted with sediment surfaces, and the reacted waste had lower alkalinity and precipitated secondary minerals. These minerals may have incorporated radionuclides as impurities, and they may have provided reactive surface sites to bind contaminant ions. The binding of contaminant ions at the solid-solution interface of sediment minerals was an important factor in determining contaminant mobility in the vadose zone. The selective surface reaction of dissolved components with indigenous mineral phases, particularly micas, contributed to radionuclide immobilization and retardation.

The study of sediment mineralogy, as it was before and after reaction with tank waste, can provide valuable insights into the mechanisms of radionuclide retardation and the potential for long-term in-ground immobilization. These aspects of waste-sediment interaction were investigated by determining the mineralogy of unaltered sediment and contrasting it with the mineralogy of synthetically altered sediments and with sediments extracted from beneath the SX tank farm. All of the sediments were examined using X-ray diffraction (XRD) and scanning electron microscopy (SEM) to provide a systematic set of observations for determining the effects of tank waste on SX sediments.

The geology of the SX tank farm is extensively summarized elsewhere (Serne et al. 2001a, b) and the stratigraphic locations are given here for reference to those summaries. The samples from the SX-108 slant borehole comprised a set of sediments that transected a tank-waste plume. The numbered samples included in this study were targeted to capture the range of chemical affects of alkaline waste on sediments from several stratigraphic horizons. The uppermost sample, 1A, originated near the interface between tank farm backfill and the Hanford Upper Sand. The next lower sample, 3A, showed the most pronounced visible effects of tank waste alteration and was stratigraphically located within the Hanford Coarse Sand sequence. Samples 4 through 14 were within the Lower Hanford Laminated Sand, and the lowermost samples were within the Hanford Plio-Pleistocene interval. The texture and mineralogy of these samples are described below.

D.2.2 EXPERIMENTAL PROCEDURES

The mineralogic composition of contaminated and uncontaminated sediments from the S and SX tank farms and nearby environment was analyzed by various methods. Some results are presented in summary here and described in greater detail in the documents cited, including uncontaminated composite samples from different locations at Hanford (Serne et al. 2001b), uncontaminated samples from boreholes 299-W22-48 (Serne et al. 2001b) and 299-W22-50 (Serne et al. 2001b), and contaminated samples from borehole 41-09-39 (Serne et al. 2001a). Samples from boreholes SX-108 slant (contaminated) and B8812 (uncontaminated) were examined explicitly for this study.

Additionally, this study investigated the mineralogic products resulting from the contact of base (NaOH) with an S and SX tank farms composite sediment. These experiments were intended to elucidate the types of mineralogic changes that could result from the reaction (base hydrolysis) of REDOX wastes (which contained high levels of free hydroxide [OH⁻]) with sub-tank sediments. The composite sediment representative of the upper Hanford formation was termed the "Above B" composite. This study material was created by compositing core samples from the depth range of 9-21 m bgs from RCRA boreholes 299-W23-14, 299-W23-15, 299-W22-46, 299-W22-39, and 299-W23-45. This same uncontaminated composite material was used in batch and column studies of Cs⁺ retardation in Section D.3.0.

D.2.2.1 Textural Analysis

Sediment samples were epoxy imbedded, wafered, polished, and mounted to glass slides. Mosaic images of the polished sections were made using backscattered electron detection in SEM. The digitized images were analyzed using Prismview image analysis software. A composite Hanford Fine Sand sample (B8814) was sieved to determine size fractions by weight percent.

D.2.2.2 X-Ray Diffraction

XRD analyses were done at PNNL and at LANL. At LANL, the instrument was a Siemens D500 diffractometer, using Cu K_α radiation with a solid-state detector. Data were collected from 2 to 70° 2θ in 0.02° increments with a 4-second step. At PNNL, the instrument was a Scintag diffractometer, using Cu K_α radiation with a solid-state detector, with operating conditions identical to those at LANL. At both laboratories, bulk samples were prepared by crushing to a powder with analysis as random mounts, and clay fractions separated by sedimentation in water were analyzed as oriented mounts, air-dried and glycol solvated. An alumina standard was used at LANL in conjunction with full-pattern fitting methods to provide quantitative mineralogical analyses. For semiquantitative analysis, various mineral standards were used at PNNL (Serne et al. 2001b). At PNNL, all phases with a nonexpansible 100 nm peak were termed "illite," at LANL such phases were termed "mica."

D.2.2.3 Scanning Electron Microscopy

Samples from SX-108 slant borehole were surveyed to assess the effects of caustic waste on sediment minerals. Samples reacted with simulated waste (NaOH) in the laboratory were

examined to determine the hypothetical effects of waste fluids on sub-tank sediments. Samples for SEM were prepared by sprinkling sediment directly onto sticky tape on a 1-inch SEM stub. For contaminated sediments from SX-108 slant borehole, a glass cylinder was rolled over the dispersed sediment to firmly fix it to the tape. This step caused some disaggregation of agglomerated clasts and mica flakes. The sediment was sputter coated with carbon for conductivity; individual clasts nevertheless exhibited poor conductivity ('charging') in some cases. Samples were imaged at PNNL using a JEOL 840 SEM. Images were captured using a Gatan CCD device and elemental analysis was via an Oxford energy dispersive spectrometer (EDS).

D.2.2.4 Sediment-Base Reaction Studies

Laboratory studies were performed to investigate the mineralogic products of base-sediment reaction using the "Above B" composite sediment from the S and SX tank farms. The sediment was pretreated by sieving to remove the less than 56 μm fraction, treated with sodium acetate, and dialyzed to equilibration with sodium bicarbonate. For each treatment, 0.8 g of **soil** was added to a polypropylene Oakridge centrifuge tube. Also, 25 mL of 1M NaNO_3 was added to each tube and the tubes were gently shaken for 30 minutes. This yielded a suspension density of 25 g/L. After shaking, the tubes were centrifuged at 2500 x G for 10 minutes and the supernatant removed and discarded. This washing process was repeated three times. After washing the sediment, the tubes were refilled with NaNO_3 solution and concentrated (10 M) NaOH to yield final concentrations of 1 M NaNO_3 , and 0.113 M, 1 M, 3 M, or 5 M NaOH and retain a suspension density of 25 g/L. The tubes were incubated at 50 °C for 14, 28, 56, or 112 days. All tubes were stored inside of sealed buckets that had a constant flow of nitrogen to preclude introduction of carbon dioxide from air. At the end of the incubation periods, sample tubes were centrifuged at 2500 x G for 10 minutes and the supernatant removed. Soils were filter washed with pH adjusted 0.01 M NaNO_3 (pH 7.5) to remove excess salt and then air-dried. Dried soils were analyzed by XRD and SEM.

D.2.3 RESULTS

D.2.3.1 Sediment Texture

The sediments had a broad distribution in grain size (Table D.2.3.1), but all were dominated by the fine fraction on the basis of grain-counting methodology (SEM image processing). At the scale of the sediment mosaics, the resolution of the analysis software was limited by the ratio of the pixel density to the smallest grain sizes: the resultant resolution limit was approximately 14 μm . The mean particle diameter was approximately uniform at ca. 37 μm , with the sediments predominated by fines having a particle diameter in the silt category (diameter less than 62 μm) or less. The samples had a large variation in grain size distributions. The standard deviations varied widely, and the grain diameter maximum ranged from 1031 μm to 334 μm . Samples 1, 3, and 5 included particularly large lithic clasts; Sample 7 was relatively uniformly fine-grained; the lower samples were coarser, and sample 17 included several large soil fragments. The dominant abundance of fines suggests that all sediment horizons should have significant reactivity with respect to alkaline tank wastes. While grain counting suggests that fines predominate, sieving and analysis according to mass shows (for a composite uncontaminated sample, Table D.2.3.1) that on a weight percent basis, the sediments are by far predominated by clasts larger than 100 μm .

Table D.2.3.1. Statistical Summary of the Grain Size Distribution for SX-108 Samples. A) Based on Digital Image Analysis of the Backscattered-Electron Mosaics. All Values in μm ; Minimum Diameters are at or Near the Minimum Measurable at the Scale of the Photomosaics. (13 mm width). B) Based on sieving, to nearest weight percent.

Sample No.		Mean Diam.	Std. Dev.	Min. Diam.	Max. Diam.
sx-10801		37.7	54.0	14.1	702
SX-108 03		41.1	71.8	14.1	1031
SX-108 05		39.4	54.2	15.5	997
SX-108 07		36.8	34.2	15.0	347
sx-108 08		37.0	47.7	13.7	768
SX-108 11		39.7	51.8	13.2	640
SX-108 13		37.4	39.1	15.0	637
SX-108 17		32.0	33.4	14.1	334
Size Fract. μm		Wt. %	Size Fract. μm	Wt. %	Size Fract. pm
>850		2	180-40	43	5-1.5
850-425		11	40-18	1	<1.5
425-180		30	18-5	3	

D.2.4 X-RAY DIFFRACTION

D.2.4.1 Pristine Sediments

Table D.2.4.2 includes typical mineralogic results, with approximate weight percent abundances from the studies of Serne et al. (2001a, b) (Note that the tabulated values are to illustrate typical relative abundances for comparison only. More detailed tabulations can be found in the references). The bulk sediment mineralogy was dominated by abundant quartz, potassium feldspar, plagioclase feldspar, and less abundant calcite. Mica was not reported. The clay mineral fraction included quartz, smectite, illite (mica), chlorite, kaolinite, and subordinate calcite and potassium feldspar.

Table D.2.4.2. Typical SX Mineralogy, Weight Percent Values, From (Serne et al. 2001a, b). Totals were not Constrained to 100Percent.

Bulk Mineralogy							
Well or Location	Quartz	K-Spar	Plagioclase	Calcite			
Site Composite	50	10	20				
299-W22-48	60	20	10	10			
299-W22-50	60	10	25				
41-09-39	50	5	50				
Clay Mineralogy							
Well or Location	Quartz	K-Spar	Calcite	Smectite	Illite	Chlorite	Kaolinite
Site Composite	5			30	40	20	5
299-W22-48	10			20	30	20	10
299-W22-50	5		10	30	15	10	10
41-09-39	10	10		5	30	20	10

The samples from borehole B8812 were examined with attention to detection of minor phases. The sediments were also size-fractionated. The Hanford Fine Sand contained laumontite ($\text{CaAl}_2\text{Si}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$), a zeolite, in fractions finer than $150\text{ }\mu\text{m}$ (Figure D.2.4.1). Analysis with attention to the overall mineralogy of phases detected at low X-ray incidence angles (e.g., zeolites and clay minerals) showed the presence of smectite, mica, laumontite, amphibole, and chlorite with variable abundance in different fractions. Other minerals occurring significantly were quartz, potassium feldspar, plagioclase feldspar, hematite, magnetite, and calcite. The abundances of these phases in bulk sediments and as a function of grain size in the sample collected at 64 ft deep are presented in Tables D.2.4.3 and D.2.4.4 respectively. Mica (biotite) increased in abundance as the mean grain size decreased; this increase may be significant for the retention of ^{137}Cs in these fractions. The XRD results from PNNL and LANL

differed with respect to the minor phases detected; bulk major minerals in all the sediments included smectite, chlorite, quartz, potassium feldspar, plagioclase feldspar, mica (whether termed illite or mica or biotite) and calcite. Kaolinite was observed in the samples examined at PNNL but not in those examined at LANL. The effort to observe minor minerals at LANL yielded identification of hematite, magnetite, amphibole, and laumontite, all at abundances of about 1 wt% or less.

Figure D.2.4.1. Comparison of Diffraction Patterns of Size Fractions of the 63.5 to 64 ft. Sample. Green Markers Show the Positions of Laumontite Reflections.

Note: The increase in smectite and chlorite content in the finest two fractions.

Table D.2.4.3. Quantitative X-ray Powder Diffraction Analyses for Bulk Samples (wt%).

Sample	Smectite	Laumontite	Chlorite	Quartz	K-Spar	Plagioclase	Hematite	Biotite	Magnetite	Amphibole	Calcite	Total
B8812 63.5-64.0' Bulk	8.5	0.2	1.2	28.4	10.2	33.8	0.2	13.2	0.4	1.2	1.1	98.3
B8812 64.0-64.5' Bulk	6.9	0.3	1.3	38.4	9.6	31.7	0.1	7.9	0.3	2.9	1.1	100.4
B8812 76.0-76.5' Bulk	8.8	0.3	1.2	38.7	8.2	32.3	0.2	6.3	0.2	3.3	0.8	100.3
B8812 76.5-77.0' Bulk	8.6	0.4	1.0	26.7	9.4	36.2	0.3	11.1	0.2	2.5	0.8	97.1
B8814 Bulk Hanford Sand	10.6	0.4	1.0	42.9	7.4	30.6	0.2	4.5	0.1	2.0	0.7	100.4

**Table D.2.4.4. Quantitative X-ray Powder Diffraction Analyses
for Sue Fractions of the B8812 63.5-64.0' Sample (wt%).**

Sample	Smectite	Laumontite	Chlorite	Quartz	K-Spar	Plagioclase	Hematite	Biotite	Magnetite	Amphibole	Calcite	Total
B8812 63.5-64.0' Bulk	8.5	0.2	1.2	28.4	10.2	33.8	0.2	13.2	0.4	1.2	1.1	98.3
825-425µm	5.2	---	1.2	46.2	9.4	31.5	0.1	5.2	0.2	1.4	0.7	101.2
425-250µm	4.3	---	1.0	45.2	8.4	32.6	0.1	6.2	0.5	1.4	0.7	100.5
250-150µm	5.8	0.3	0.9	40.2	8.9	32.4	0.2	5.8	0.9	1.8	1.1	98.3
150-75µm	7.5	0.5	1.3	37.4	8.0	37.0	0.2	5.9	0.7	2.1	0.9	101.6
75-45µm	7.5	0.6	1.1	34.5	9.4	34.4	0.1	8.2	0.1	2.4	1.1	99.4
45-18µm	9.4	1.1	1.7	33.4	9.2	34.3	0.1	5.4	0.5	2.8	2.5	100.4
18-5µm	14.7	0.8	3.2	25.2	9.2	30.3	0.1	11.3	0.3	1.4	2.9	99.4
5-1.5µm	24.9	0.9	5.2	18.5	9.9	26.1	0.2	10.4	0.1	0.9	3.0	101.1
1.5-0.25µm	52.7	0.6	3.2	7.1	7.9	17.5	0.1	10.1	0.0	0.5	2.6	102.1

D.2.4.2 Base-Reacted Sediments

Diffraction patterns for 5 M base-reacted sediments indicated that there was no zeolite in these samples. The diffraction patterns suggested the presence of a zeolite phase (Figure D.2.4.2), either tetranatrolite ($\text{NaAl}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$) or an unnamed phase ($\text{Na}_{14}\text{Al}_{12}\text{Si}_{13}\text{O}_{51} \cdot 6\text{H}_2\text{O}$). Close examination of the figure revealed an imperfect match between the zeolite library diffraction files and the reacted sediment, a possible result of chemical/structural differences between the precipitated phase and the library phases. Alternatively, the observed diffraction peaks may have come from feldspars in the bulk sediment. XRD results for the bulk reacted sediment were similar to those for the bulk pristine sediment, with coarse-grain mineralogy consisting of **quartz**, potassium feldspar, and plagioclase feldspar (the sediments had been sieved to remove fines less than 75 µm in diameter.)

Figure D.2.4.2. Diffraction Patterns for Bulk Post-Reaction Samples from Sediment-Base Reaction Experiments. Result Suggest that a Na-Zeolite is Present.

D.2.4.3 Tank SX-108 Samples

Three samples from tank SX-108 were intensively studied to identify possible effects of waste interaction on sediment mineralogy. Figure D.2.4.3 compares a pristine sample from borehole BB8812 with SX-108 samples 3A, 6A, and 7A. The same major minerals were present in the pristine **and** contaminated sediments, as was laumontite. Chabazite, a calcium-bearing zeolite, may have been present in sample 7A only. Also present in 7A, and perhaps in 6A was the secondary mineral nitratine, NaNO_3 , a likely precipitate from tank wastes. Mica, chlorite, amphibole, and smectite were definitively identified in the clay fraction (Figure D.2.4.4), and kaolinite may have been present. All of these phases were also observed in the pristine samples. A comparison of SX-108 sediments with a pristine sample (Figure D.2.4.5), with overlain peak markers for tetranatrolite and the unnamed hydrated sodium aluminum silicate, indicated that these zeolitic phases were not present. Potential library-sample matches for them could be explained by other common phases such as feldspars.

Figure D.2.4.3. XRD of Three Contaminated Samples and One Pristine Sample (offset for clarity).

Note: The presence of a small amount of laumontite in all samples, plus the possible presence of chabazite in Sample 7A. Chabazite has not been identified in any pristine sample. Inset shows the presence in 7A of nitratine, NaNO_3 .

Figure D2.4.4. Diffraction Patterns of the Clay Fraction of Samples 3A, 6A, and 7A, after Solvation with Ethylene Glycol.

Note: The presence of mica (denoted by biotite), chlorite, an amphibole (denoted by magnesioriebeckite), and smectite, shown by the broad peaks centered around $5.5^\circ 2\theta$. The peak just above $25^\circ 2\theta$ has a low-angle shoulder, suggesting the presence of kaolinite in these samples. Although present in the bulk samples of 3A, 6A, and 7A, laumontite (and chabazite in 7A) is not apparent in the clay fraction of these samples.

Figure D.2.4.5. A Portion of the XRD Patterns for Altered Samples 3A, 6A, and 7A, with that for the Pristine Sample from 76.5 to 77' Depth. The Latter Pattern has been Displaced Vertically for Clarity. Peak Markers for Tetranatrolite (red) and for Hydrated Na-Al Silicate (green) are Superimposed at the Bottom.

Note: That where potential matches to these phases exist, they exist in both pristine and altered samples and are due to other common phases such as feldspars.

D.2.5 SCANNING ELECTRON MICROSCOPY

D.2.5.1 Pristine Sediments

SEM inspection of uncontaminated sediments from borehole B8812 allowed the identification of minerals whose abundance was too low for detection by bulk XRD. These minerals were observed in very small quantities. In addition to minerals identified by XRD, barite, Fe-oxides, rutile, pyroxene, apatite, zircon, and rare-earth-element minerals were identified. Fe-oxides were observed on the surfaces of some micas.

D.2.5.2 Laboratory Base Reacted Sediments

Sediments reacted with base in the laboratory ("Above B" composite) were considered to be representative of subsurface sediments and the possible types of mineral surface reactions and secondary mineralization products that might be observed in waste-impacted sediments. Three sets of images are presented as illustrations of the mineral transformations observed in the laboratory.

Micas were drastically altered by NaOH (Figure D.2.5.6). The surfaces and edges of the mica were encrusted with secondary minerals, and the edges were dulled by dissolution and weathering. Distinctive clusters of zeolitic minerals were precipitated (Figure D.2.5.7). These took the form of starred clusters and balls, but also included cemented aggregates of plates and blades. Zeolites also formed distinctive colonies and clusters on mineral surfaces (Figure D.2.5.8). The secondary phases formed radiating clusters, cluster aggregates, and singular balls on mica surfaces. These phases were apparently not detected by XRD (see discussion above), indicating that they did not compose a significant mass fraction of the sediment.

Figure D.2.5.6. Micas Altered During Base Interaction Experiments. **Figure D.2.5.7. Zeolite Crystals Formed During Base Interaction Experiments.**

Figure D.2.5.8. Zeolites Precipitated on Mineral Surfaces During Base Interaction Experiments.

D.2.5.3 SX-108 Samples

Samples 1A, 3A, SA, 7A, SA, 11A, 13A, and 17A from the SX-108 slant borehole were examined (all with S0070 prefixes). The first four of these samples included high activities of ^{137}Cs . The highest activity was observed in sample 7A ($2.14 \times 10^7 \text{ pCi g}^{-1}$). Sample 3A also contained high levels of ^{137}Cs ($1.95 \times 10^7 \text{ pCi g}^{-1}$) and was chalky in appearance, suggesting mineral alteration.

Three attributes that were clearly evident by electron microscopy were used to assess the chemical impact of tank leakage on sediments: the development of secondary mineralization on sediment clasts, the occurrence of clay-cemented agglomerates of clasts, and the alteration of mica. The latter was a sensitive indicator of chemical alteration. In pristine samples (e.g., 13A) the micas were clear of surface-precipitated secondary minerals, and the edges of individual lamina were sharp and clean. In altered micas, flake surfaces were covered with fine aluminosilicate precipitates, and edges were blunt and obscured by secondary mineralization. The formation of cemented agglomerates was also indicative of alteration but was not diagnostic. In the notably altered sample 3A, agglomerations of silicate clasts were abundant. Agglomerates were also present but were sparse in deeper, apparently unaltered sediments; their abundance was the important discriminator in sample 3A. The abundance of secondary mineralization was also apparently higher in waste-impacted sediments. In these sediments, silicate clasts such as quartz and feldspar were abundantly coated with secondary aluminosilicates. The compositions of

these secondary minerals were consistent with those of quartz and smectite. Smectite (an aluminosilicate clay mineral with minor Fe, Mg, Ca, and Na) was the apparent cement for agglomerates, which always contained a significant mica component. Other secondary phases had compositions that included silicon oxide, iron oxide, calcium phosphate, and aluminum silicate: these were presumably quartz, iron oxide, apatite, and kaolinite, all observed in XRD studies. Secondary minerals occurred in close heterogeneous association of very fine individual grains.

The occurrence of smectite as a product of interaction with alkaline wastes was not apparent in XRD studies. The poor crystallinity of this mineral and the preexisting smectite in unreacted sediments could have prevented its detection by the relatively insensitive XRD method. The synthesis of smectite by exposure to alkaline wastes is consistent with the experimental synthesis of smectites from mineral and oxide components in alkaline conditions (Deer et al. 1976b). Zeolite is common in altered volcanic rocks and volcanic sediments, and these minerals were expected in waste-impacted sediments, but only very rare occurrences of minerals that could be zeolites were observed in these samples.

Figures D.2.5.9 through D.2.5.19 illustrate mineral alteration, top-to-bottom through the borehole. The photomicrographs present examples of the alteration indicators described above. The uppermost four samples, 1A, 3A, 5A, and 7A show unmistakable indications of interaction between tank waste and sediments.

Figure D.2.5.9. Sample LA. 4A. Feldspar with Secondary Minerals on Surface. A. Smectite, B. Silica. 4B. Agglomerated Clasts Cemented by Secondary Clay. Bladed Mica is Abundant, with Subordinate Silicates.

Figure D.2.5.10. Sample 1A. Mica Edge, and Detail (right) Showing Absence of Alteration.

Figure D.2.5.11. Sample 3.4. 6A. Agglomerated Clasts Disaggregated During Mounting. A: Plagioclase Feldspar; B: Smectite; C: Mica; D: Potassium Feldspar. 6B. Clay-Cemented and Coated Clasts. Larger Clast (A) is Coated with Smectite; Agglomerated Clast Includes Quartz (B) and Mica (C).

Figure D.2.5.12. Sample 3A. 7A. Very Altered Mica. Lamella are Curled and Altered (A), Surface is Weathered and Coated with Secondary Smectite. 7B. Altered Mica Edge. Delaminated Flake Revealed the Contrast Between the Unaltered and the Extensively Altered Edges and Surface. The Surface is Coated with a Masking Layer of Secondary Smectite (A). The Edges of Mica Flakes are Splayed and Blunted by Chemical Alteration and Deposition of Secondary Phases.

Figure D.2.5.13. Sample 5A. Detail of Unaltered Mica Edge.

Figure D.2.5.14. Sample 7A. Cemented Agglomerate of Smectite and Mica, with an Associated Grain of and Sodium-Aluminum-Silicate (EDS spectrum) that may be Zeolite.

Figure D.2.5.15. Sample 7A. 10A. Altered Mica. Secondary Mineralization on the Surface is not Extensive, but Edge Alteration is Evident. 10B. Unaltered Mica with Few Associated Surface Smectite Grains. Edges are Sharp and Unaltered. This Morphology Predominates.

Figure D.2.5.16. Sample 8A. 11A. Detail of Unaltered Mica, Showing Deformed, Sharp, Unaltered Edges. Some Smectite Adheres to the Surface 11B. Unaltered Mica, some Srneetite Adheres to Surface, Edges are Unaltered.

Figure D.2.5.17. 12A, Sample 11A. Unaltered Mica. 1212, Sample 13A. Unaltered Mica.

Figure D.2.5.18. Sample 17A. 13A. Several Clasts, A: Potassium Feldspar, B: Unaltered Mica, C: Smectite Cemented Agglomerate Including Mica. 13B. Unaltered Mica. Edges are Rent but Sharp and Unaltered, and there is no Surface Precipitated Secondary Mineralization. Compare to the Mica in Figure D.2.5.12.

Figure D.2.5.19. Comparison Between SX-108 Sample 03, Quartz Grain with Surface Zeolite Grains, and Zeolite Clusters on a Quartz Grain after a Sediment-Base Interaction Experiment. Natural Samples have much Sparser Occurrence of Zeolite.

Sample 1A (Figures D.2.5.9 and D.2.5.10) showed moderate effects of interaction, with some secondary minerals on silicate surfaces and some agglomeration. Micas, however, were unaltered.

Sample 3A (Figures D.2.5.11 and D.2.5.12) showed the most pronounced effects of tank waste reaction; the texture of this sample resembled crumbled concrete. Primary silicates were abundantly coated with silica and what appeared to be smectite, producing elemental lines on energy-dispersive X-ray spectra of varying intensities for Si, Al, Na, and Ca, with or without minor inclusion of Fe and Mg. These heterogeneous accumulations of minerals on clast surfaces may include detrital and secondary smectites or poorly crystalline aluminosilicates, with the secondary minerals incorporating differing proportions of their component oxides. These minerals were carefully examined for crystal morphology and chemistry comparable to the zeolites observed in the laboratory experiments with waste simulants (e.g., Figures D.2.5.7 and D.2.5.8 and Figure D.2.5.6, especially cruciate morphology of Na-Al-Si-O composition.) Unambiguous zeolite crystals were not observed. The similarity of components between smectite and Na-zeolite may have hindered the identification of a Na-zeolite if its morphology were not well developed. The morphology of some of the agglomerated crystallites in Figure D.2.5.8A were similar to those observed in the sediments reacted in the laboratory with waste simulants. However, the sediments reacted in the laboratory were sieved to remove the less than 56 μm size fraction. The formation of zeolite may have been masked in the SX-108 samples by the inclusion within or overprecipitation by more abundant aluminosilicate. If a Na-zeolite were present, its abundance was very low, much less than 1 wt%, because Na-rich secondary mineral fragments were very rare and of micron-scale. Agglomerates were common, and varied in the fractional inclusion of smectite cement; some agglomerates were readily disaggregated into discrete constituent clasts, some were more indurated. The presence of abundant secondary aluminosilicate and the abundant smectite-cemented agglomerates may be responsible for the chalky texture of this sediment.

Micas in sample 3A were pervasively altered. The platelets were curled and crenellated (Figure D.2.5.12A), and flake surfaces were generously plated with secondary minerals (Figure D.2.5.12B). Some mica flakes were so altered that they could be mineralogically identified only with the aid of compositional data. Comparison of the altered micas from 3A with the experimentally altered micas (presented above) shows a close similarity. As with smectite, the alteration of micas did not produce a change in XRD results to reflect lower mica abundance (see above). Although mica surfaces were altered, the flake interiors were not (Figure D.2.5.12), so that XRD intensities were not noticeably changed.

Sample 5A was relatively unaltered. Clast surfaces had little secondary mineral deposition. Agglomerates were rare. Micas were unaltered (Figure D.2.5.13). This sample with ^{137}Cs of $6.52 \times 10^6 \text{ pCi g}^{-1}$, was between 3A, extensively altered and ^{137}Cs activity of $1.95 \times 10^7 \text{ pCi g}^{-1}$, and 7A, with moderate alteration and the highest ^{137}Cs activity ($2.14 \times 10^7 \text{ pCi g}^{-1}$). This relatively unaltered interval with lesser activity was probably a result of borehole and waste-migration geometry. The borehole was essentially a one-dimensional transect of a three-dimensional waste plume. The plume was not necessarily compact and monolithic in shape, and the borehole seems to have intersected a portion of the subsurface that was less impacted by leaking waste.

Sample 7A (Figures D.2.5.14 and D.2.5.15) was moderately affected by interaction with tank wastes. There was limited secondary mineralization on clast surfaces, agglomerates were few, and micas were unaltered. This interval within the SX-108 slant borehole had the highest ^{137}Cs activity, but was much less altered than sample 3A.

Samples 3A and 7A, on close examination in conjunction with autoradiography results (see Section D.3.5 “Mineralogic Residence of ^{137}Cs in Contaminated Sediments”), showed evidence for the precipitation of zeolites on mineral surfaces. In comparison, however (Figure D.2.5.19), the secondary zeolite-like phases on natural samples are far fewer and less developed than zeolites on experimentally reacted solids.

Samples 8A, 11A, 13A, and 17A (Figures D.2.5.16 through D.2.5.18) were unaltered, and had activity one or more orders of magnitude lower than 1A, 3A, 5A, and 7A. Agglomerates occurred sparsely. Micas in these intervals had little surface-adhering minerals, and the mica edges were sharp and unaltered. The contrast with 3A is evident in comparing Figure D.2.5.18 with Figure D.2.5.12. The 3A mica had bent lamina with blunted edges and a dense surface coating of secondary phases; the 17A mica also had bent lamina, but the edges were sharp and no secondary phases were present.

The micaceous minerals in sample 3A were pervasively altered but sample 3A still retained significant ^{137}Cs , presumably in the relatively unaltered portions of micas. While this sample suffered the most alteration of any examined, a lower sample, 7A, retained the highest mass-normalized level of ^{137}Cs activity. Sample 7A, however was only moderately impacted by caustic waste. These results indicated strong and rapid retardation of OH^- by mineral reaction. If base neutralization by mineral reaction was responsible for the differences in the extent of mineral alteration and secondary mineralization, the reaction was not reflected in the pH of 1:1 suspensions with water. The four upper samples (1A, 3A, 5A, and 7A) retaining significant ^{137}Cs all had suspension pH above 9 (9.16, 9.58, 9.78, and 9.55, respectively; data from Serne, elsewhere in this document). Samples below 7A had slurry pH of approximately 8 by comparison.

D.2.6 CONCLUSIONS AND IMPLICATIONS

Minor mineralogic differences were observed between sediments of differing stratigraphic origin or history of exposure to authentic or simulated tank waste. The differences were primarily in the variability of the relative masses of minerals rather than changes in mineralogic identity. Minor differences were also noted between mineralogic analyses performed at PNNL and LANL. The X-ray diffraction analysis provided a common set of mineral phases in the pristine sediments, base-reacted sediments, and SX-108 core samples. Other than nitratine, NaNO_3 , apparently precipitated from tank wastes in sample 7A, there was no definitive determination using X-ray diffraction of the addition of a secondary mineral phase to the SX-108 sediments after reaction with tank wastes.

The mineralogy determined by XRD was consistent, regardless of the exposure to alkaline solutions. Within the precision of measurement, the following minerals were present (abundances in weight percent): quartz, 35; potassium feldspar, 10; plagioclase feldspar, 35; mica (biotite or muscovite), 10; smectite, 10. The separation and analysis of clay or silt-sized particles added the detection of minor (generally less than 1 wt% in the bulk) laumontite, kaolinite, amphibole, magnetite, hematite, chlorite, and calcite. Because they are highly crystalline and occur with low surface-to-volume ratios, quartz and the feldspars would not be expected to react extensively with transient alkaline waste. The low reactivity of these phases was supported by SEM results. Smectite is poorly crystalline and theoretically unstable, eventually reacting to form kaolinite (depending on solution composition). However, in the presence of reacting minerals supplying abundant dissolved ions, alkaline conditions favored the formation of smectite and zeolites. The appearance of mica surfaces suggested that micas reacted preferentially, and that a secondary aluminosilicate (perhaps smectite) formed mica surfaces.

The experimental reaction of representative sediments with high concentration of NaOH apparently resulted in the formation of a secondary Na zeolite as suggested by SEM analyses. Zeolite formation is favored in alkaline environments because high pH favors the increased solubility of silica in solution (Newman 1987). Zeolites are also common weathering products of basic (e.g., basaltic) rocks (Deer et al. 1976a), which form a significant fraction of the waste-impacted sediments. The unambiguous identification of the secondary zeolite in experimentally reacted sediments was obscured in XRD results by abundant primary feldspar in the samples, but the morphology and chemistry of secondary phases observed in SEM was consistent with a Na-zeolite. Extensive XRD examination of SX-108 sediments did not show the production of detectable secondary zeolites, and XRD patterns from pristine and impacted sediments were indistinguishable. Again, very minor amounts of a Na aluminosilicate phase were observed that may have been a secondary zeolite.

The experimentally reacted sediments had been size fractionated (fines were removed) prior to reaction, and the secondary zeolites stood out on the surfaces of primary silicates. In the impacted SX-108 sediments, the presence of zeolites may have been obscured by the presence of abundant preexisting smectite, and waste-induced secondary phases that might be zeolite were of low abundance and indistinct morphology. By examining the surfaces of individual clasts with very low ^{137}Cs activity, some secondary phases with the appropriate composition were found. These phases were far too sparse to have affected the results of bulk or clay-size XRD.

The secondary 'zeolites' were present, however, and apparently retained a small, detectable quantity of radiation (see Section D.3.5). The difference in results from the two exposures to high concentrations of NaOH — i.e., the purposeful laboratory experiment and the accidental leakage exposure — may also be largely due to the stark contrast in the conditions of reaction. In the zeolite-producing laboratory experiments, the solids-solution ratio was very low, so that the pH was relatively constant throughout the course of the experiment (e.g., the OH reactant was in excess). Beneath the SX tank farm, the solids-solution ratio was very high so that the pH would be rapidly moderated by base-induced hydrolysis of the mineral fraction. The conditions under the tank may thus have had only a transient potential for zeolite precipitation.

Tank wastes altered the sediment composition and mineralogy, generating non-crystalline or poorly crystalline reaction products. These secondary phases were not apparently abundant enough to be detected by XRD, but may have been significant in affecting the behavior of ^{137}Cs . Sample 3A was altered to an extent that affected its appearance and texture, and samples 1A and 7A were also significantly altered. Sample 5A was apparently little impacted and showed few effects of having contacted tank waste; it was apparently in a location that had been impacted little by leaking wastes. The chemical reaction of tank wastes with sediments did not correlate directly with the retention of ^{137}Cs .

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D.3.0 GEOCHEMISTRY AND REACTIVE TRANSPORT BEHAVIOR OF ^{137}Cs

^{137}Cs ($t^{1/2} = 30.07$ y) is a high-yield fission product existing in tank wastes at Hanford in significant concentrations (e.g., 10^{-1} - 10^0 Ci/L). The supernatant concentration of ^{137}Cs in the leaked S-SX single-shell tanks (SSTs) has been estimated to range between 3.05×10^{-5} mol/L - 3.91×10^{-4} mol/L in tanks SX-108, SX-109, and SX-115 (Jones et al. 2000). Single-shell tank leakage in the S and SX tank farms has released approximately 86.9 kCi of ^{137}Cs to the vadose zone in highly alkaline, highly saline (NaNO_3 - NaNO_2) waste solutions, although in-ground inventory estimates vary considerably between authors using different estimation methods and/or assumptions (Jones et al. 2000). All estimates, however, reinforce the fact that ^{137}Cs is the major in-ground radioactive inventory element in the S and SX tank farms, with additional large in-ground inventories site-wide.

Many previous engineering-based measurements of Cs adsorption to Hanford sediments have shown that the migration of Cs in the Hanford subsurface is strongly retarded by ion exchange reactions. It is also known that electrolyte cations (e.g., Na, Ca, Mg, and K) influence Cs migration in Hanford sediments through competitive ion effects, and empirical relationships describing these effects over certain electrolyte concentration ranges have been established. However, the observed subsurface migration of ^{137}Cs beneath the S and SX tank farms is deeper than expected given this knowledge base and current conceptual models of fluid migration in the Hanford vadose zone (Ward et al. 1997). Great concern exists over the future behavior of the enormous in-ground ^{137}Cs inventory. Should corrective measures be applied in the S and SX tank farms, and other tank farms where Cs subsurface contamination is extensive (e.g., B-BX-BY) to prevent its future migration? Of particular concern is whether the extensively sorbed in-ground Cs pool is exchangeable with the aqueous phase and susceptible to remobilization by infiltrating meteoric waters or dilute waste fluids released during tank sluicing.

A series of research activities was performed to provide a more comprehensive understanding of Cs geochemistry and reactive transport in sediments from the S and SX tank farms, because existing information was inadequate to interpret the in-ground concentration profiles of ^{137}Cs in sediments obtained by the spectral gamma logging of dry wells (DOE-GPO 1996) and direct analyses of core materials beneath leaked tanks (e.g., 41-09-39, SX-108 slant). The new research has involved both Hanford S&T Program and EMSP investigators and includes use of uncontaminated and contaminated subsurface sediments from the S and SX tank farms. The overall objectives of this research have been to provide scientific insights on (1) waste characteristics and reactive transport phenomena that have produced the current in-ground distribution of ^{137}Cs and (2) the susceptibility of sorbed Cs to future migration. The results and implications of this research are described in the following sections: adsorption reactions of Cs in WMA S-SX sediments in presence of high-salt and base, spectroscopic studies of Cs-containing micas to define chemical and structural controls on Cs adsorption, reactive transport experiments and modeling under saturated and unsaturated conditions, mineralogic residence of ^{137}Cs in contaminated sediments, and lability and desorption of the in-ground ^{137}Cs pool.

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D.3.1 ADSORPTION REACTIONS OF CS IN WMA S-SX SEDIMENTS IN PRESENCE OF HIGH SALT AND HIGH BASE

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D.3.1.1 Introduction

The sorption of Cs to geologic materials has been well studied by the scientific community (e.g., Cornell 1993). Cs engages in ion exchange reactions with hydrated cations on the planar sites of smectites and vermiculites and is strongly and selectively sorbed to frayed edge sites (FES) that develop along the weathered periphery of micas (e.g., biotite and muscovite). Multisite adsorption models have been developed that include this phenomenology (Brouwer et al. 1983; Poinssot et al. 1999). The sorption behavior of Cs^+ in a geologic material is a sensitive consequence of the relative concentrations of smectite/vermiculite and mica/illite as the former are the primary contributors of planar sites, and the latter of the strongly sorbing FES.

Hanford sediments contain small but significant concentrations of Cs-sorbing phyllosilicates (smectites and micas) that are ubiquitous components of the Hanford formation flood deposits and underlying Ringold formation. It has long been recognized that Hanford sediments have a strong sorption potential for Cs. Performance assessment models have been used to forecast Cs migration at Hanford using distribution coefficients (K_d s) estimated from empirical regression equations involving sediment cation exchange capacity (CEC), electrolyte composition/concentration, and Cs retention at tracer concentration (e.g., 10^{-9} - 10^{-8} mol/L). Mobility predictions from these models have been adequate for dilute waste streams where Cs is highly retarded (e.g., many disposal cribs), but appear to be inadequate for application to the S and SX tank farms where Cs^+ , Na^+ , K^+ , and OH^- concentrations were high in the leaked waste fluids and Cs migration was more substantial. The waste concentrations of the above ions were in significant excess to those where previous measurements have been made on the sorption of Cs^+ to Hanford sediments.

Here we report on new studies of Cs^+ adsorption to WMA S-SX sediments that were performed over concentration ranges of Cs and other ions selected to bracket those present in leaked REDOX wastes from the S and SX tanks. An experimental design was followed that allowed parameterization and testing of a multisite, multicomponent ion exchange model to compute Cs adsorption (e.g., K_d) from REDOX-like waste solutions. Following model development, other experiments were performed to quantify (1) the impacts of **high** OH^- on Cs adsorption that might result from near-field waste-sediment reaction (base-induced dissolution and reprecipitation of clay-sized materials) and (2) ^{137}Cs ion exchange behavior in contaminated WMA S-SX sediments. Last, the multisite ion exchange model was applied to Cs distribution data from the SX-108 slant borehole to provide insights on in situ retardation mechanisms. Comprehensive results of these studies may be found in Zachara et al. (2001), Ainsworth et al. (2001a, b), and several other papers in preparation.

D.3.1.2 Experimental Procedures

D.3.1.2.1 Sediment Collection and Analysis. The “Above B” Hanford formation medium/fine sand composite (D.2.2) was used as an experimental medium. The particle size distribution and mineralogy of this sediment is described by Zachara et al. (2001). The composite was divided into two subsamples, with one subsample receiving multiple extractions with pH 4.5 Na-acetate (NaOAc-treated) to remove sodium and calcium carbonates. The other sample was used without specific treatment other than ion saturation with Na^+ , K^+ , or Ca^{2+} electrolyte.

The mineralogy of the bulk sediment, separated clay and silt fractions with appropriate ion saturation, and hand-picked micas were determined by X-ray diffraction using “research quality procedures.” The cation exchange capacity of NaOAc-treated sediment was determined using Na^+ , Ca^{2+} , or K^+ saturated material. Isotopic exchange with either ^{22}Na or ^{45}Ca in 0.002 mol/L NaNO_3 or 0.001 mol/L $\text{Ca}(\text{NO}_3)_2$ electrolytes, respectively, was used to determine the surface excess of these cations. The aqueous phase activity of ^{22}Na and ^{45}Ca after 16 hours equilibration was determined by liquid scintillation counting. The K^+ exchange capacity of the sediment was measured by extracting with 0.1-mol/L ammonium acetate. The K^+ concentration in the extract was measured by inductively coupled argon plasma emission spectroscopy.

D.3.1.2.2 Cs Adsorption Experiments. Cesium sorption isotherms on NaOAc-treated “Above B” sediment were measured in NaNO_3 , KNO_3 , and $\text{Ca}(\text{NO}_3)_2$ electrolytes of various concentrations. Solids were presaturated with the appropriate electrolyte before addition of CsNO_3 . The solids concentrations in Na electrolyte were 100 g/L, 50 g/L, 10 g/L, and 2 g/L in 7.0/5.0, 1.0, 0.1, and 0.01 mol/L NaNO_3 , respectively. The solids concentrations were varied between 100 g/L and 2 g/L depending on electrolyte concentration and identity to achieve statistically sound sorption measurements. Cesium nitrate concentrations ranged from 10^{-9} to 10^{-1} mol/L, and were labeled with 7×10^3 to 2.00×10^4 dpm/mL ^{137}Cs . The suspensions were shaken in 50 mL high-density polyethylene bottles at 80 rpm and 30 °C for 16 hours. Solid-liquid phase separation was accomplished by centrifugation (5000 rcF for 30 minutes). The ^{137}Cs in the aqueous phase was determined by gamma counting. The suspension pH was measured using a calibrated glass combination electrode.

D.3.1.2.3 Effect of High Base on Cs Adsorption. The leaked REDOX wastes in WMA S-SX are believed to have contained in excess of 1 mol/L free OH^- (Lichtner 2001). Hydroxide is highly reactive with aluminosilicate minerals. Two types of experiments were performed to evaluate whether OH^- in REDOX wastes may have altered the Cs adsorbability of the Hanford sediment.

In the first experiment, “Above B” composite sediment was contacted with 0.1 mol/L NaOH (in 1 mol/L NaNO_3 at 40:1 liquid:solid ratio) in Teflon containers at 10 ° and 50 °C under $\text{N}_{2(g)}$ atmosphere. The OH^- concentration yielded a $\text{pH}_c = 13.2$ and a computed pH of 12.6. The sediment was removed after 56, 112, and 168 days of contact and washed repeatedly with pH 8 electrolyte of decreasing concentration. The reacted sediment was air-dried after soluble salts were removed, and Cs adsorption isotherms were measured in 1 mol/L NaNO_3 , as described above, at 25 °C. The results allowed evaluation of whether CEC and adsorption site distribution and affinity for Cs were changed by base reaction.

The second experiment investigated the sorption of Cs during OH⁻/sediment reaction. Three series of replicate Teflon tubes containing “Above B” sediment were spiked with 3 mol/L carbonate-free NaOH (the approximate free O H in tank SX-108) in 1 mol/L NaNO₃. Each tube series was then spiked with one of three concentrations of Cs (10⁻⁹, 10⁻⁷, 10⁻⁵) and equilibrated with shaking at 50 °C under N_{2(g)} atmosphere. Replicate tubes were sacrificed at different times out to 120 days, and the aqueous phase analyzed for Cs, Al, Fe, Si, K, Ca, and several other ions. Only results for Cs will be reported here. Other base-weathering&-reaction studies were performed at different temperatures and O H concentrations, and results are reported in Ainsworth et al. (2001).

D.3.1.3 Results

D.3.1.3.1 Mineralogy and Cation Exchange Capacity. The cation exchange capacities (CEC) of the “Above B” composite varied with saturating ion (Table D.3.1.1) and were relatively low because the small amount of clay (less than 2%). The higher CEC in K⁺ was consistent with the presence of a micaceous mineral fraction, but its large excess over that in Ca²⁺ and Na⁺ electrolyte was not easily explained. The CEC measurements were repeated six times to ensure reproducibility. The Na CEC of the composite was very similar to the measured CECs of (1) uncontaminated Hanford fine sands from borehole W22-48 (Serne et al. 2001a), and (2) contaminated Hanford fine sands from boreholes 41-09-39 and SX-108 slant (Table D.3.1.2).

Table D.3.1.1. Cation Exchange Capacities and Cs⁺ Sorption Maxima in Different Electrolytes.

Index ion	CEC (eq/g × 10 ⁻⁵) n = 6	Max Cs adsorption (eq/g × 10 ⁻⁵) ^a n = 4
Na ⁺	4.26 +/- .12	5.79
K ⁺	8.25 +/- .35	3.61
Ca ⁺	4.69 +/- .14	6.22

^aObserved in the lowest ionic strength of each electrolyte.

	Na-CEC (eq/g)	Comment
Above-B composite	$4.26 \times 10^{-5} \pm .12^a$	Composite of Hanford fine sands from RCRA boreholes on east and west sides of WMA S-SX
$\begin{array}{c} \times \\ \times \\ \times 10^{-5a} \\ \times \\ \hline 10^{-5} \end{array}$		
4-61	$4.2 \pm 0.3 \times 10^{-5b}$	Hanford fine sands from W22-48,
91.5	$4.8 \pm 0.4 \times 10^{-5b}$	
101.5	$6.0 \pm 0.4 \times 10^{-5b}$	

^aMeasured by ^{22}Na isotopic dilution.

^bMeasured by NH_4Cl displacement.

The weight percentages of the mineral constituents varied with particle size. The mineralogic analysis of the bulk sediment showed that quartz was the dominant mineral phase with lesser amounts of plagioclase and potassium feldspars, micas, chlorite, and smectite. Micas, including muscovite, biotite and vermiculitized biotite, were present in all size fractions of the sediment. The feldspar content decreased with decreasing particle size. Most of the feldspar was plagioclase with anorthite being the dominant phase. The clay fraction consisted of smectite, vermiculite, chlorite, and mica. The Mg saturated, glycol-solvated clay displayed an intense but very broad diffraction maxima for smectite. X-ray diffractograms of the clay-sized fraction of the "Above B" sediment were almost identical to the clay-sized fraction of contaminated samples from boreholes 41-09-39 (Seme et al. 2001b) and SX-108 slant (data not shown).

D.3.1.3.2 Cs^+ Adsorption Chemistry from Na^+ , K^+ , and Ca^{2+} Electrolytes. The adsorption isotherms of Cs^+ in Na^+ and K^+ electrolytes were dependent on electrolyte concentration (Figure D.3.1.1). Electrolyte concentration was less important with Ca^{2+} . The isotherms were of the Freundlich type with slopes below unity (Freundlich $1/n$ less than 1), implying sorption site heterogeneity. Cs^+ adsorption from K^+ electrolyte was the most linear of those studied (e.g., isotherm slope = 0.85 to 0.95). Increasing salt uniformly displaced the isotherms in both Na^+ and K^+ electrolyte, indicating adsorption by ion exchange.

Figure D.3.1.1. Cs^+ Adsorption Behavior on the "Above B" Sediment Composite From WMA S-SX Presented as Adsorption Isotherms $[(\text{Cs})_{\text{ads}} \text{ versus } (\text{Cs})_{\text{aq}}]$, Exchange Isotherms $[\text{E}(\text{CsX}) \text{ versus } \text{E}(\text{Cs-aq})]$, and K_d Functions $[\text{K}_d \text{ versus } (\text{Cs})_{\text{aq}}]$.

The adsorption data were reformatted in terms of surface (E) and aqueous ($\tilde{E}$) equivalent fractions where

$$E_{Cs} = q_{Cs}/Q \text{ and } \tilde{E}_{Cs} = [Cs^+]/\tilde{Q} \quad (D.3.1.1)$$

where q_{Cs} was the adsorption density in mole/g, Q was the electrolyte specific CEC (e.g., Table D.3.1.1), $[Cs^+]$ was the aqueous concentration in mole/L and $\tilde{Q}$ was the total solution normality. The Cs^+ adsorption data for the monovalent exchange systems (Na^+ , K) reduced to single exchange isotherms over wide ranges in surface and aqueous equivalent fractions [$\log E_{CsX}$ versus $\log \tilde{E}_{Cs(aq)}$], while three parallel but distinct ion exchange isotherms resulted for Ca^{2+} electrolyte (Figure D.3.1.1).

The distribution ratio, K_d [(L/g) = (mol Cs^+ /g)/(mol Cs^+ /L)], is a parameter used to describe sorption strength in radionuclide performance assessment models. Here, K_d decreased with increasing salt concentration and the total Cs concentration (Figure D.3.1.1). The effect of increasing Na^+ and K^+ were generally comparable. The decrease in K_d with total Cs concentration was smallest in K^+ electrolyte, but was as much as 2 to 3 orders of magnitude in Na^+ and Ca^{2+} electrolyte. At high salt (Na^+ and K) and Cs^+ concentrations (e.g., greater than 10^{-4} mol/L), adsorption was negligible [e.g., K_d (mL/g) = 0]. The competitive effect of the electrolyte ions on Cs^+ sorption followed the trend $K^+ \gg Na^+ \geq Ca^{2+}$.

D.3.1.3.3 Ion Exchange Modeling. Conditional equilibrium constants (K_c) for Cs^+ exchange were computed from the data in Figure D.3.1.1 according to the following relationships.

$$uCs^+_{(aq)} + AX_u = uCsX + A^{u+}_{(aq)} \quad (D.3.1.2)$$

$$K_c = [A^{u+}][E_{CsX}]^u/[Cs^+]^u[E_{AXu}] \quad (D.3.1.3)$$

where $A^{u+} = Na^+, K^+, \text{ or } Ca^{2+}$ and $[\]$ is concentration. E_{CsX} (the equivalent fraction of Cs^+ on the exchange fraction) was defined as in equation (D.3.1.1) and E_{AXu} as $1 - E_{CsX}$. The resulting K_c s were equivalent to the Vanselow model for homoionic, monovalent exchange (e.g., $Na^+ - Cs^+$, $K^+ - Cs^+$), and to the Gaines and Thomas model for heterovalent exchange (e.g., $Ca^{2+} - Cs^+$ see Sposito 1981).

The K_c s increased as the fractional occupancy of the CEC by Cs^+ decreased (Figure D.3.1.2). In monovalent electrolyte, K_c increased abruptly below $E_{CsX} = 0.01$, while K_c in Ca^{2+} electrolyte showed a monotonic increase with decreasing equivalent fraction of Cs^+ . All experiments showed a leveling or approximately constant K_c below a $\log E_{CsX} = -4.5$. The magnitude of these K_c values in the three electrolytes and their trend with respect to adsorption density were similar to those reported for illites (Brouwer et al. 1983; Comans et al. 1991).

Figure D.3.1.2. Computed Condition Equilibrium Constants (K_c) From Figure D.3.1.1 and Results of Multisite Modeling (Lines) with Best-Fit Parameters (Site Concentrations Expressed as a Fraction of the CEC, and Binary Ion Exchange Constants) as Noted.

A multisite ion exchange model was applied to the adsorption data (Figure D.3.1.2, solid lines). The model is fully described in Zachara et al. (2001). In the multisite model, the adsorbed concentration is hypothesized to result from the contributions of sorption sites that differ in both affinity (e.g., high and low) and concentration. The measured electrolyte specific CECs (e.g., Table D.3.1.1) were used as the total site concentrations. Previous multisite modeling of Cs^+ adsorption to illite rationalized these different sites as existing on the phyllosilicate basal plane and the frayed edge. The concentration (of Cs) and ionic strength dependence of the homovalent exchange ($\text{Cs}^+ - \text{K}^+$ and $\text{Cs}^+ - \text{Na}^+$) was well approximated by a two-site model (Figure D.3.1.2). A one-site model could not reproduce the sorption data from any electrolyte. The primary electrolyte ions in REDOX wastes (K^+ and Na^+) were competitive with Cs^+ for both high- and low-affinity sorption sites.

Modeling the heterovalent exchange ($\text{Cs}^+ - \text{Ca}^{2+}$) was more challenging and required five distinct sites to adequately fit the data (Figure D.3.1.2). This difficulty in describing $\text{Cs}^+ - \text{Ca}^{2+}$ ion exchange was not considered to be especially significant to the S and SX tank farms, because Cs^+ migration trails the Ca^{2+} plume that was displaced by Na^+ from the ion exchange complex.

D.3.1.3.4 Effects of High Base. Equilibration of the “Above B” sediment with 0.1 mol/L NaOH/1 mol/L NaNO_3 leads to a progressive increase in CEC with contact time (Table D.3.1.3), presumably through base-induced hydrolysis and exfoliation of micas. The measured isotherm data on the base-treated sediments was recast as K_{cs} calculated according to Equations D.3.1.1 through D.3.1.3, using the new CEC data (Figure D.3.1.3a). The “0-day” data in Figure D.3.1.3a was the same as that plotted for 1 mol/L NaNO_3 in Figure D.3.1.2. Base treatment had a surprisingly small impact on Cs sorption selectivity to the sediment after the observed increase in CEC was accounted for. There was a slight reduction in K_{c} below an equivalent fraction of 10^{-3} (0.2 to 0.25 log units) that increased with base contact time, indicating a lessening in the exchange selectivity of the FES for Cs. This experiment and others in this series indicated that base reaction changed the mineralogy of the clay fraction, but had minimal influence on the overall sorptivity of Cs.

**Table D.3.1.3. Measured CEC Value of
“Above-B” Composite After Reaction with
0.1 mol/L NaOH at 50 °C.**

Contact time (d)	CEC ^a (eq/g)
56	$4.71 \pm 0.12 \times 10^{-5}$
112	$6.73 \pm 0.11 \times 10^{-5}$
168	$7.42 \pm 0.89 \times 10^{-5}$

^aCEC measured by ^{22}Na isotopic dilution, n = 3.

Figure D.3.1.3. Selected Results of Base Reaction Studies with "AboveB" Composite.

Note: a) K_c values for Cs⁺ adsorbed to sediment contacted with 0.1 mol/L NaOH at 50 °C for various time periods. The sediment was washed free of reaction products before adsorption was measured at 25 °C in 1.0 mol/L NaNO₃. b) Temporal behavior of Cs sorption when added with 3 mol/L NaOH. The suspension was equilibrated at 50 °C.

All kinetic studies of Cs sorption to Hanford sediment have shown that the ion-exchange reaction occurs rapidly, within the time frame of hours. Some small increases or decreases in Cs sorption relative to the initial ion exchange reaction have been observed with prolonged contact time (e.g., 10 to over 100 days). These long-term changes have been attributed to intraparticle diffusion (increases) and K^+ release through mineral dissolution (decreases). The temporal behavior of Cs sorption in presence of high base (3 mol/L, 50 °C) was markedly different from these past observations (Figure D.3.1.3b). A rapid initial reaction was observed (less than 1 day), followed by a decrease (1 to 24 days), then another increase in Cs adsorption (55 to 110 days). The concentrations of Si, Al, and K^+ in particular, were quite dynamic over this time period indicating an effect of mineral dissolution and precipitation reactions. It is not yet known whether the sorbed state after 110 days in terms of mineral residence and desorbability is similar to that after the initial reaction (1 day). The sediment at experiment termination showed signs of significant mineral alteration and was similar in many respects to sample 3A from the SX-108 slant borehole. This experiment differed from that in Figure D.3.1.3a in that a higher base concentration was used (3 mol/L as compared to 0.1 mol/L) and Cs^+ was present in solution as mineral phases dissolved and precipitated.

D.3.1.3.5 Ion Exchange of ^{137}Cs in Contaminated WMA S-SX Sediments. Four samples of ^{137}Cs -contaminated sediment from 41-09-39 and SX-108 slant were placed in Na^+ , K^+ , and Rb^+ electrolytes of three different concentrations and equilibrated for 6 days to determine if the sorbed ^{137}Cs was exchangeable. Literature reports indicate that cation selectivity on phyllosilicates generally follows the trend: $Cs^+ \cong Rb^+ > K^+ \gg Na^+$ (e.g., Brouwer et al. 1983; Zachara et al. 2001). It was therefore expected that Rb^+ and K^+ would be effective in displacing ^{137}Cs .

The ^{137}Cs aqueous concentrations that resulted were dependent on electrolyte identity and concentration (Figure D.3.1.4); a significant fraction of the sorbed Cs pool was exchangeable with the aqueous phase. Increasing the electrolyte concentration led to an increase in desorbed ^{137}Cs through ion exchange. Consistent with the higher affinity of K^+ and Rb^+ for the FES, these ions were more effective than Na^+ in displacing adsorbed ^{137}Cs . Between 19 and 26.9% of the adsorbed ^{137}Cs was displaced by the highest concentrations of K^+ and Rb^+ (Table D.3.1.4).

Figure D.3.1.4. Observed and Predicted Ion Exchange of ^{137}Cs in Contaminated WMA S-SX Sediments After 6 Days Equilibration in Different Electrolyte Solutions.

Note: Electrolyte concentrations noted immediately below bars. The predicted values include the assumption of, 1) 100% exchangeability or, 2) partial exchangeability to provide best data fit. a) Na⁺ Electrolyte, b) K⁺ Electrolyte, and c) Rb⁺ Electrolyte.

Table D.3.1.4. Exchange of ^{137}Cs From Contaminated S-SX Sediments Using Different Electrolytes.

Sample	Total ^{137}Cs pCi/g (std dev)	Measured ^{137}Cs Exchange pCi/g (% of total)			Predicted ^{137}Cs Exchange		
		5.0 mol/L Na^+	3.4 mol/L K^+	3.4 mol/L Rb^+	Na	K	Rb
					100% ^a	100% ^a	100% ^a
7A	5.94×10^7 (1.34×10^7)	3.04×10^6 (5.12)	1.13×10^7 (19.0)	1.34×10^7 (22.4)	(.84) ^b	(.28) ^b	(0.25) ^b
3A	3.42×10^7 (1.30×10^6)	1.44×10^6 (4.21)	6.87×10^6 (20.1)	8.03×10^6 (23.5)	6.08 (4.66)	69.7 (19.1)	98.6 (24.6)
7A/B/C	4.01×10^7 (1.04×10^6)	1.87×10^6 (4.66)	8.43×10^6 (21.0)	1.08×10^7 (26.9)	7.01 (2.30)	76.3 (21.1)	99.1 (24.8)
9A/B/C	2.37×10^6 (1.10×10^5)	1.13×10^5 (4.76)	5.03×10^5 (22.4)	5.98×10^5 (25.2)	5.10 (4.27)	67.8 (19.7)	91.9 (23.0)

^aPredicted described amount of ^{137}Cs by multi-site model assuming entire adsorbed Cs pool is exchangeable in 6 hours.^bPredicted described amount of ^{137}Cs by multi-site model assuming the noted fraction of the adsorbed Cs pool is exchangeable in 6 hours.

The analytically determined isotopic ratio of ^{137}Cs in the aqueous phase of these equilibrations [$^{137}\text{Cs}/(^{137}\text{Cs} + ^{135}\text{Cs} + ^{133}\text{Cs}) = 0.2083$], the computed total Cs concentration in the sediment given this abundance value, and the ^{137}Cs activity determined by high-performance germanium counting (HPGe), the CEC measured by ^{22}Na dilution (Table D.3.1.2), and the indigenous ion content of the aqueous and exchanger phases determined by 1:1 water extraction and NH_4^+ displacement, respectively, were used as input to the equilibrium multisite exchange model to predict the expected $^{137}\text{Cs}_{(\text{aq})}$ concentrations in the different electrolyte solutions (Figure D.3.1.4). The model used the exchange constants ($K_{\text{K-Cs}}$, $K_{\text{Na-Cs}}$, and $K_{\text{K-Na}}$) and site fractions calculated for the “Above B” composite (Figure D.3.1.3), and a $K_{\text{Rb-Cs}}$ estimated from Brouwer et al. (1983). The calculations were first performed with the assumption that all the sorbed Cs was exchangeable over the 6 hours experimental period. This assumption led to calculated $^{137}\text{Cs}_{(\text{aq})}$ concentrations that were remarkably close, albeit slightly above the observed values in the Na electrolyte (Figure D.3.1.4a; Table D.3.1.3) given the uncertainty in the ^{137}Cs activity determined by HPGe (error bars). The predicted concentrations for the K^+ and Rb^+ electrolytes significantly exceeded the observed values (Figures D.3.1.4b, c; Table D.3.1.3) but their computed decrease with decreasing electrolyte concentration paralleled the observed trend.

The fraction of exchangeable Cs was adjusted to determine if the model calculations could be improved by assuming a constant value of labile Cs for the sample suite as a whole. Cs may diffuse into the dehydrated, interlamellar regions of phyllosilicates with long contact times (Comans et al. 1991). The fraction of Cs undergoing such diffusion is slowly exchangeable with the aqueous phase. The data was best described by assuming that 84% of the adsorbed Cs was exchangeable in Na electrolyte and 25 to 28% was exchangeable in K and Rb electrolytes. Given these assumptions of exchangeability, the $^{137}\text{Cs}_{(\text{aq})}$ concentrations were well described with the multi-site model using parameters developed on the “Above B” composite (Figure D.3.1.4; Table D.3.1.3). The calculations for the Rb electrolyte showed deviations at the intermediate electrolyte concentration that were attributable to the use of a $K_{\text{Rb-Cs}}$ that was not specific to the Hanford sediment. Undoubtedly, the Rb calculations could be improved by the measurement of a Hanford specific value. Other measurements of Cs exchangeability and a discussion of causes and implications are provided in other subsections of this Appendix (Ainsworth et al. 2001).

D.3.1.3.6 ^{137}Cs Retardation in WMA S-SX. The multisite model parameters for Cs^+ , K^+ , and Na^+ summarized in Figure D.3.1.2 were used along with (1) the average CEC for contaminated Hanford fine sands from WMA S-SX (4.62×10^{-5} eq/g; Table D.3.1.2) and (2) the computed free concentrations of Na^+ and K^+ in SX-108, SX-109, and SX-115 tank wastes (Lichtner 2001) to compute K_d functions for Cs in the sub-tank sediments (Figure D.3.1.5a). The calculation shows that Cs retardation is a strong function of its adsorption density, which, in turn, is dependent on the total Cs^+ concentration. For SX-108 and SX-109 wastes, the K_d is virtually 0 above an adsorbed concentration of 10^{-7} mol/g. Adsorbed Na^+ and K^+ block Cs adsorption to all but the high affinity FES sites because of their high aqueous concentration. Because ^{137}Cs represents only 20.83% of the total Cs concentration, the figure suggests that the maximum ^{137}Cs sorption capacity of the Hanford fine sand in presence of SX-108 and SX-109 supernate is reached at approximately $1.5 \times 10^8 - 3.0 \times 10^8$ pCi/g ^{137}Cs . These computed values are remarkably close to the highest adsorbed ^{137}Cs concentrations observed in sediments from the SX-108 slant borehole that were collected closest to the tank (1A - 3.7×10^8 pCi/g; 3A - 1.39×10^8 pCi/g). If it

assumed that the underlying Hanford fine sand has a bulk density of 1.4 g/cm^3 and a porosity of 0.3, and it becomes saturated with tank SX-108 waste ($3.05 \times 10^{-5} \text{ mol/L Cs}$) and adsorbs 90% of the Cs, then the adsorbed Cs concentration would be approximately $1.22 \times 10^{-9} \text{ mol/g}$ of ^{137}Cs or $1.46 \times 10^7 \text{ pCi/g } ^{137}\text{Cs}$. This adsorption density is an order of magnitude below the estimated sorption capacity and is close to the high-end values of sorbed ^{137}Cs noted in deeper core samples from both 41-09-39 and SX-108 slant.

The lower salt concentrations in tank SX-115 allow significantly greater Cs retardation in Hanford fine sands surrounding this tank (e.g., increases in K_d by 3x; Figure D.3.1.5a). For example, a finite K_d (2.5-3.5 ml/g) is observed over an adsorption density range of 10^{-7} to 10^{-5} mol/g as a result of partial Cs^+ accessibility to planar sites on smectites and vermiculites. This lower affinity ion exchange allows for a larger adsorption maximum of ^{137}Cs (approximately $2.0 \times 10^{11} \text{ pCi/g}$). Given this higher retardation potential, it is not surprising that ^{137}Cs was not observed in the borehole proximate to SX-115 (299 W23-19; Serne et al. 2001c).

The multisite model was also used along with the average CEC of the contaminated Hanford fine sands ($4.62 \times 10^{-5} \text{ eq/g}$; Table D.3.1.2), the porewater concentrations of Na^+ and K^+ computed from the 1:1 water extraction data of SX-108 (Serne et al. 2001d), and the total Cs determined by direct gamma counting to compute in situ K_d values for comparison with those observed (Serne et al. 2001d). The computed ^{137}Cs - K_d values matched the observed ones quite well in trend over the whole borehole (Figure D.3.1.5b), and were close in value between 80 to 100 feet where the highest Na and K concentrations were found in porewater. Significant deviations were observed in upper region (55 to 71 feet) of the ^{137}Cs accumulation zone (55 to 88 feet), where aqueous Na concentrations were low ($0.103\text{--}0.313 \text{ mol/L}$) and where mineral alterations as a result of heat and base reaction were observed (Section D.2.1). Variations in CEC beyond the average value ($4.62 \times 10^{-5} \text{ eq/g}$), changes in ion exchange affinity as a result of mineral alteration (e.g., $K_{\text{Cs-Na}}/K_{\text{Cs-K}}$), and partial Cs fixation within phyllosilicates armored by secondary precipitates are potential causes of discrepancy. Overall, however, the surprisingly good agreement between the computed and observed K_d values suggests that the current in-ground distribution of ^{137}Cs is in approximate ion-exchange equilibrium with the pore water and phyllosilicate sorbents in the sediment phase.

D.3.1.4 Conclusions and Implications

- (1) Although Hanford sediments have a high potential to adsorb Cs^+ by selective ion exchange, Na^+ and K^+ are competitive ions that exist in the REDOX wastes that act to strongly suppress Cs^+ sorption even at trace levels. Subsurface mobility is enhanced beyond previously expected values.
- (2) The competitive effects of Na^+ and K^+ and the strong concentration dependency of Cs^+ sorption could be well described by an equilibrium, multisite ion exchange model. The model was parameterized using the "Above B" composite sample representative of the sediments in the 12 m below the S and SX tank farms.

Figure D.3.1.5. Multisite Model Simulations Using Site Fractions and Exchange Constants From "Above B" Sediment, Model Calculations of REDOX Tank Waste Composition, and Cs Distribution Data Below SX-108.

*Calculation was based on previous 2-site equilibrium sorption model and measured aqueous Na, K, and Cs concentrations in SX-108 slant borehole sediments. The CEC was fixed at 4.62×10^{-5} (eq/g).

Note: a) Computed & functions for SX-108, 109, and 115 tank waste solutions and b) predicted versus observed in situ K_d values for ^{137}Cs below SX-108.

- (3) Reactions of $[\text{OH}^-]$, a highly reactive waste component, with the S and SX sediments did not markedly change their sorption behavior for Cs. High base reaction increased the CEC of the sediment by approximately 30%. After accounting for the effect of CEC increase, the ion exchange selectivity was found to decrease only slightly after base reaction at 50 °C.
- (4) A significant fraction (greater than 20%) of the adsorbed Cs pool in tank-waste contaminated sediments **was** exchangeable with the aqueous phase and desorbable by Na^+ , K^+ , and Rb^+ . The multisite model that had been parameterized using the "Above B" composite provided good semiquantitative predictions of Cs release from, and equilibrium concentrations in contact with, contaminated S and SX sediments. Model calculations indicated that an unresolved fraction of adsorbed Cs was less exchangeable with the aqueous phase.
- (5) The trend and magnitude of the in situ K_{ds} for ^{137}Cs beneath tank SX-108 conform generally to multicomponent ion exchange predictions. It appears that the existing in-ground distribution of ^{137}Cs is in approximate ion exchange equilibrium with its solid and aqueous phase surroundings.

Ion exchange experiments with Cs on WMA S-SX sediments showed that the high concentrations of Na^+ and K^+ present in REDOX wastes may have expedited subsurface Cs transport by reducing attenuation and the effective K_d to low values. Uncertainty in the total and free concentrations of both Na^+ and K^+ in the actual leaked solutions prevents more precise statements. However, more recent modeling of the S and SX tank waste solutions indicates Na concentrations were even higher than initially thought and may have reached 19.6 mol/L for tank SX-108 (Section D.7.3). These high concentrations of Na are consistent with the deep penetration of ^{137}Cs . Our findings indicated that sorbed ^{137}Cs in contaminated S and SX sediments is partially labile and its measured aqueous and solid phase distribution appears to conform to an equilibrium state with respect to ion exchange. This current chemical condition is one that undoubtedly evolved over time. It is not necessarily proposed that the in-ground distribution of ^{137}Cs is reflective of an equilibrium transport event at the time of waste emplacement. Growing evidence suggests that the waste emplacement event may have been quite rapid. Unsaturated transport experiments show that Cs breakthrough is more rapid than expectation under low moisture content and high flux rates (Section D.3.4). Collectively these studies indicate that the chemical effect of high salt is probably just one of several factors that allowed deep penetration of strongly sorbing Cs.

A sizable fraction of the adsorbed ^{137}Cs pool in contaminated **WMA** S-SX sediments was replaceable by Na^+ , K^+ , and Rb^+ (see also Section D.3.6). While these results indicated that much of the sorbed Cs pool is available for transport, they do not necessarily imply that future migration is expected or probable. We employed very high concentrations of the electrolyte ions that were near saturation with their respective NO_3^- salts to induce mass-action displacement of ^{137}Cs . It is inconceivable that such high concentrations of K^+ or Rb^+ would ever occur in the Hanford vadose zone. Sodium was less effective in displacing adsorbed ^{137}Cs , but is a ubiquitous ion in the vadose zone originating from tank waste discharge and mineral water reaction. Currently, the Na^+ pulse resulting from tank waste leakage **has** migrated beyond/deeper

than that of Cs, with more dilute waters following. These dilute waters stabilize ^{137}Cs in the exchange complex and limit desorption.

Our results suggest that future migration of ^{137}Cs is unlikely unless Na concentrations in porewater approach those in the original REDOX waste discharge (e.g., 10 mol/L). Realistic scenarios to achieve such concentrations are few, but do include “leak-losses” from tank sluicing designed to dissolve salt-cake. Leak-losses should not induce ^{137}Cs mobilization if kept sufficiently dilute, and the waste sluicing process should be managed with this issue in mind. The adsorption data and models developed in this section can be used to identify concentration ranges of sluicing solutions that can be safely leaked to the vadose zone without fear of Cs mobilization.

D.3.1.5 Acknowledgement

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D.3.2 SPECTROSCOPIC STUDIES OF CS-CONTAINING MICAS

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D.3.2.1 Introduction

The micas, including biotite and muscovite in Hanford sediments, have a crystallographic structure that strongly binds poorly-hydrated monovalent cations such as Cs^+ . This structure consists of metal ions, principally Al and Si but including isomorphous substitutions of Fe and other metals, in sheets where they are octahedrally and tetrahedrally coordinated with O. These sheets are bound together by K to form a book structure; platy flakes of mica are common components of sedimentary rocks, and are plentiful in the unconsolidated sediments at Hanford. The retention of Cs^+ by micas has been intensively studied using contaminated sediments and laboratory specimens (Comans et al. 1991; Comans and Hockley 1992; Evans et al. 1983; Francis and Brinkley 1976; Sawhney 1970). The resultant conceptual model of the controls on Cs^+ mobility in the environment includes rapid initial and slower continued adsorption, with complimentary dual rates of desorption. Typically, a fraction of adsorbed Cs^+ is intransigent to desorption after an extended residence on the mica surface. The model relies on deductions about different binding sites on the mica surface that have not been documented by direct measurement. These include basal-plane exchange sites, chemically frayed sites at flake edges, and interlayer sites where Cs^+ could displace and substitute for K^+ . The significance of the latter binding reaction (diffusion of Cs^+ into interlayer space by displacement of K^+) has been questioned, since solid phase diffusion constants yield infinitesimally slow rates of less than 1 nm per year (Comans et al. 1991).

We carefully examined the spatial residence of Cs^+ on the surfaces and the interiors of Hanford mica flakes to establish the relevance of the conceptual model to the different types of mica found in the Hanford and Ringold formations. Our methods were directed at several questions about the conceptual model and the classes of binding sites on the different mica surfaces. First, was Cs^+ preferentially sorbed to edge sites? If binding to frayed edge sites was stronger than binding to sites on the basal plane, then Cs^+ should be concentrated there. Second, are sites internal to mica flakes accessible to aqueous Cs^+ ? If these sites were accessible, then the reactive surface area on a mica flake would be much larger than would be estimated by consideration of the area on the edges and basal surfaces of a mica flake alone. We also hoped to observe the diffusive penetration of Cs^+ into interlayer space if it occurred more rapidly than calculated from theoretical considerations.

Our experiments could have significance for determining the fate of contaminant ^{137}Cs at Hanford. For instance, if we observed a heterogeneous localization of Cs at particle edges, the hypothesis of strong binding at edges would be confirmed. Strong binding to particle edges and rapid intraparticle migration (our experiments were short-term) would suggest that desorption and mobilization to future infiltrating waters or waste solutions would proceed slowly.

D.3.2.2 Experimental Procedures

Micas were hand picked from uncontaminated Hanford formation fine sands (35 to 55 ft below ground surface) collected during placement of RCRA monitoring wells around the S and SX tank farms boundary. Three phases were differentiated on the basis of color and morphology: clear muscovite, rust vermiculite, and black biotite. Small numbers of flakes were exposed to varying concentrations of CsNO_3 (0.001, 0.01, and 0.08 M) for 28 days, then washed in deionized water and air-dried. Some of the flakes were then mounted to glass slides (exposing the basal plane), while others were imbedded in epoxy and fixed to glass slides as polished, ca. 50 μm -thick thin sections, cut normal to the basal plane. All samples were sputter-coated with carbon to assure electrical conductivity.

The detection of Cs on solid surfaces relied on two types of spectroscopy. Electron microprobe (EMP) analysis used wavelength dispersive spectroscopy (WDS). X-ray microprobe (XMP) analysis used WDS and energy dispersive spectroscopy (EDS), alone and in combination. Both spectrophotometric methods detected induced, characteristic X-radiation. The WDS method relied on Bragg diffraction to eliminate interference from other elements by using a crystal of known d-spacing. Its advantage is a high resolution and low background, but it detects a single element at a time. The EDS discriminated between X-radiation from different elements on the basis of photon energy. Its advantage is the ability to detect and monitor a wide range of elements at once, but it has relatively poor bandwidth and a higher background than WDS.

The EMP analysis on a JEOL 8600 instrument used WDS spectrometers with 30 eV resolution that were tuned to wavelengths for Cs, K, and Fe $K\alpha$ radiation and left fixed during image acquisition. The samples were examined using an accelerating potential of 20 KeV and a beam current of 20 nA, with the electron beam focused to ca. 50-nm on the sample surface. The beam position was digitally controlled and a digital compositional image of the sample was acquired by rastering the beam over the sample surface at, typically, 100-nm steps with a beam dwell time of 500-ms per step; images were collected overnight.

The x-ray microprobe measurements were performed at the PNC-CAT insertion device beamline (Heald et al. 1999) and at the GSE-CARS beamline, both at the ANL Advanced Photon Source (APS). Focusing was achieved using Kirkpatrick-Baez mirrors. The entrance slits were set at 0.7×0.7 mm and the beam focused to 5 μm horizontally $\times$ 6 μm vertically. Typical flux was about 5×10^{11} ph/sec. The sample was rotated 30-degrees from normal incidence giving an effective horizontal spot of about 6- μm . The beam energy was selected with a Si (111) double crystal monochromator with an energy resolution of $\Delta E/E = 1.4 \times 10^{-4}$. The fluorescence from the sample was detected at PNC-CAT using either a 13-element solid-state detector with typical energy resolution of about 300 eV alone, or in combination with a bent Laue crystal detector (WDS) with 30 eV resolution. At GSE-CARS a tunable WDS detector identical to that used in EMP measurements was used. The Laue crystal detector was tuned to the Cs L_{α} fluorescence line, and was able to detect about 5×10^9 Cs atoms in the beam spot. Energy windows on the 13-element detector were set to record the fluorescence signals from K, Ca, Ti, Cr, Mn, and Fe as the sample was scanned. For imaging, the incident energy was set to 7110 eV. This only partially excites the Fe signal, avoiding detector saturation from high concentrations of Fe. The detection limit at GSE-CARS was approximately 1-ppm on a mass basis. Weight percent

concentrations were not measured. The detection of Cs was judged against background, and comparative results were obtained by examining and equalizing brightness levels between sample background areas.

D.3.2.3 Results

The laboratory-prepared mica samples with adsorbed Cs^+ were first examined by EMP. Micas that were exposed to different concentrations of CsNO_3 did not show discernible differences in surface concentrations; the images shown here all originated from the 0.08 M CsNO_3 suspensions. Figure D.3.2.1 is a plan view of biotite, vermiculite, and muscovite flakes, imaged according to the surface concentration of Cs and K. The three mineral species did not retain Cs equally. Biotite retained the highest quantity and had the highest spot concentrations, with Cs distributed very heterogeneously. The vermiculite surface had at best gentle gradations in Cs retention, which was very low. (During laboratory manipulation of "vermiculite" flakes, the surfaces readily delaminated, revealing a "biotite" core. The surface layers of vermiculite were not judged to be a barrier to solution contact with the biotite surface, and vermiculites were not studied further.) Of the micas examined, muscovite retained the least amount of Cs^+ .

Figure D.3.2.1. Electron Microprobe Elemental Images of Cs-Exposed Micas.

Note: Lower images of K abundance serve well as overall images of morphology. Cs is most abundant at flake edges, and is most abundant where K is depleted. Lower images of K abundance serve well as overall images of morphology. Cs is most abundant at flake edges, and is most abundant where K is depleted.

The Cs images in Figure D.3.2.1 were adjusted digitally for comparison purposes: the background intensity of each image was adjusted to a uniform level so that the relative brightness (Cs concentration) could be observed. The pattern of retention on the mica surfaces

indicated that edge sites strongly sorbed Cs^+ . The altered edges in biotite and muscovite showed the highest concentrations. The basal plane sites also retained some Cs^+ , as shown by the brightness above background across each flake. The images showing flake morphologies are the complimentary intensities of K radiation for each image. These images were adjusted digitally to best show the contrast of K concentrations within each flake, (e.g., to give a range of black-to-white in each image). On biotite and muscovite, Cs intensities were highest where K was depleted (dark areas in the K images). This was consistent with the hypothetical chemical "fraying" of edges through K^+ depletion, to provide sites with high adsorption affinity for Cs^+ . The abundance of iron may also be a positive covariant with Cs.

Figure D.3.2.2 presents comparative images of the (unadjusted) intensities of K, Cs, and Fe for biotite and muscovite. As observed in Figure D.3.2.1, the biotite surface was depleted in zones where Cs was concentrated. Fe also appeared to be in higher concentration where Cs was present, although the relationship was general; e.g., Fe was broadly more abundant on the right of the biotite flake where Cs was present in patchy concentrations. Because Fe was relatively abundant in biotite, subtle variations in its concentration—as correlated with Cs—were not readily apparent in these X-ray images. The relationship between Fe and Cs on the muscovite flake was easily seen, even though the intensities were lower. The muscovite was very thin, showing apparent transparency in the K image, and Fe was present at low concentrations typical of muscovite. The muscovite image was collected at twice the spatial resolution of the biotite. The relationship between K depletion and Cs abundance was obscured by the mottling caused by the abrupt and significant differences in thickness across the flake, but there was a clear correlation between the abundance of Fe and Cs. This relationship could be the result of weathering that solubilized K and perhaps Si, leaving areas abundant in frayed edge sites and insoluble Fe(III).

Samples that were sectioned normal to the C axis after exposure to Cs^+ were used to investigate whether Cs^+ could access the interiors of mica flakes (Figure D.3.2.3, for muscovite). The K image clearly showed structural splaying of the mica edge by weathering. Cs was concentrated at the ends of weathered plates, but was also present above background on the flake interior in the relatively unweathered core (the possible presence of natural Cs in micas was investigated at the PNC-CAT—data not shown—and no detectable Cs was present in natural biotites or muscovites). Again, a correlation of Cs adsorption density with elevated Fe concentrations was observed. Fe has low abundance in muscovite, and the brightness levels in the image were manipulated to enhance contrast.

Figure D.3.2.2. Comparison of K, Cs, and Fe on the Surfaces of Biotite and Muscovite.

Note: Cs is concentrated where K is depleted and where Fe is enriched. The bottom of the biotite image was partially clipped during data collection. The muscovite image was collected at double the spatial resolution as the biotite image, and the muscovite flake is so thin near the bottom that it appears translucent.

Figure D.3.2.3. Muscovite Section Imaged as K, Cs, and Fe Abundance.

Note: The Mica Flake is weathered and its component plates are splayed where it has been most severely altered. Cs is distributed at the edges of Mica Plates. Fe and Cs are correspondingly enriched near the platelet ends.

There is an inherent difficulty in the use of EMP to define structural locations for metal adsorption (Figure D.3.2.3). Although the optical resolution of the images was high, the detection limit, defined by the ability to perceive Cs above background, was near the level at which Cs^+ was adsorbed. The Cs image in Figure D.3.2.3 was manipulated to show variations in abundance, but the contrast between background and signal was low. Investigations of the internal distribution of Cs in micas required a much lower detection limit, as supplied by the synchrotron-based technique, XMP. XMP provides great elemental sensitivity, but generally poor optical resolution; in some cases the inability to simultaneously monitor multiple signals is problematic. Figure D.3.2.4 allows a comparison of Cs distribution in sectioned biotite as mapped by EMP and XMP. The relatively low-magnification EMP image provided good detail of the distribution of Cs at edges and interlamellar channels, while the higher-magnification XMP image showed a continuum of Cs abundance with a local maximum within interlamellar space.

Figure D.3.2.4. (a) Electron Microprobe (EMP), and (b) X-ray Microprobe (XMP) Images of Cs⁺ Distribution in Cross-Sectioned Biotite (brighter false colors denote higher abundance).

Note: Cs⁺ localizes in select surface and edge regions, and in Interlamellar Channels. XMP provides far greater sensitivity.

The lower detection limits and the consequent increased range of abundance measurements afforded by XMP provided confirmation of the distribution of Cs with respect to morphologic features on flake surfaces. On muscovite (Figure D.3.2.5), Cs was concentrated at flake edges and along fractures or cracks on the muscovite surface. In cross section (Figure D.3.2.6), Cs was detected at an estimated operational detection limit of 1-ppm. This image showed several important details of Cs distribution, highlighted by detail insets. At the flake's edge, there are many zones of Cs localization; this is a confirmation of the observed concentration of Cs near the flake edge in Figure D.3.2.3. The sensitivity of XMP showed that these zones were discrete and spatially compressed. Also identified were laterally continuous zones of high Cs⁺ adsorption density in the flake interior. These indicated that dissolved Cs⁺ was able to access high-energy sorption sites in portions of the flake interior. This result was not expected, since solid-state diffusion limitations would prevent Cs⁺ from accessing the interior in the absence of cracks or micro-fissures that would allow fluid transport. As seen dimly in the optical image, the flake has some internal open areas and Cs⁺ may have been channeled to the flake interior along cracks and delamination features.

Figure D.3.2.5. Optical Image of Muscovite Flake with Cs Abundance Overlay.

Note: Cs is most abundant at edges and along cracks on the flake surface. Blue is an indication of Cs below detection, white is maximum abundance. The XMP image is 1.3-mm across.

Figure D.3.2.6. The Abundance of Cesium Within a Muscovite Flake.

Note: The sectioned flake is ca. 1.2-mm long. Cs is concentrated at platelet edges on the ends of the flake, and within restricted zones in the flake interior.

The distribution of Cs within biotite flakes (Figure D.3.2.7) was similar to muscovite, but the relationship of Cs adsorption density to biotite's more complex chemistry was not clear. As with muscovite, Cs was concentrated at edges, flake ends, and along internal fissures. Cs was more abundant where K was depleted, as previously observed. However, Cs was also more abundant where either Ti or Fe were abundant. Both Fe and Ti are primary components of biotite, and the observed association could be related to the extent of alteration. Ferrous iron may have been dissolved and removed, or dissolved, oxidized, and precipitated to form zones of increased abundance; the weathering process could have formed zones of Fe enrichment or depletion. For Ti, however, dissolution and removal are unlikely, so the apparent enrichment of Ti may be an artifact of more extensive weathering, or the minor inclusion of a Ti specific phase such as ilmenite. If enriched Fe and Ti are taken as indicators of a molecular-level weathering environment, the relationship of Cs with Fe and Ti was consistent with the hypothesized binding of Cs at frayed edge sites.

Measurements of Cs distribution in contaminated samples from tank SX-108 were attempted. Detector sensitivity measurements using a liquid sample indicated a yield of 200 cts/sec when the X-ray beam illuminated 9×10^{10} atoms; the detection limit was taken as ca. 5×10^9 Cs atoms within the beam. The tank SX-108 sample 07 had approximately 10^{14} Cs atoms, which, if homogeneously distributed, would present ca. 5×10^7 atoms to the beam. A concentration factor of about 100 was thus required to reach the detection limit, and Cs was not detected. The calculations of Cs abundance may have been marginally incorrect and the necessary concentration factor was apparently not achieved.

D.3.2.4 Conclusions and Implications

Our experiments demonstrated that Cs^+ was rapidly sorbed by micas extracted from the SX tank farm sediments. Biotite and muscovite each sorbed Cs^+ , but biotite was more effective than muscovite. The adsorption behavior of Cs^+ in Hanford sediments has been modeled with a two-site model containing sites of high affinity (mica edges) and low affinity (phyllosilicate basal planes), as described in Section D.3.1. After short contact in our experiments, Cs^+ was concentrated at edge sites on mica particles and penetrated the mica flakes along planes of delamination and fractures to bind to sites in the flake interiors. The Cs was concentrated at high-energy sites that represented a small fraction of the total surface area. This work confirms the existence on micas of high-energy sites capable of sorbing and immobilizing contaminant Cs^+ from tank waste leakage. The examination of contaminated sediments from SX-108 slant borehole, using microscopy and autoradiography, confirmed the importance of micas in immobilizing ^{137}Cs (Section D.3.5). The ability of Cs^+ to access high energy sites internal to mica flakes markedly enhances the sorption capacity of micas, provides a transport limitation to desorption, and increases the overall immobilization of Cs^+ in these sediments.

D.3.2.5 Acknowledgement

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Figure D.3.2.7. XMP False Color Images of Sectioned Biotite: 780 × 165 Microns.

Note: Chemical abundances normalized to the color spectrum are, top to bottom, Cs, Ti, Fe, Mn, and K. Cs is concentrated where K is depleted and either Ti or Fe are enriched.

D.3.2.6 References

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D.3.3 REACTIVE TRANSPORT EXPERIMENTS INVESTIGATING THE MIGRATION OF ^{137}Cs IN SEDIMENTS BENEATH THE HANFORD SX TANK FARM

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D.3.3.1 Introduction

Recent observations in the S and SX tank farms show that cesium (^{137}Cs) has migrated to greater depths than expected (Seme et al. 2001a, b). Various explanations for enhanced Cs migration include: (1) physical processes such as fast flow pathways or bypassing of exchange sites in immobile zones, and (2) chemical processes associated with the very high salt contents and high pH of the tank fluids. Ion exchange processes are clearly indicated in the depth profiles of ^{137}Cs , and potassium (K), sodium (Na), calcium (Ca), and nitrate (NO_3 , acting as a tracer) from the boreholes beneath tank SX-108 and tank SX-115. Below both tanks, Cs concentration peaks are retarded with respect to K and Na. The importance of cation concentration on ion exchange is clearly illustrated by the Na and tracer profiles beneath the tanks. Pore water with high Na concentrations at tank SX-108 showed little or no retardation of Na, as indicated by superimposed Na and NO_3 peaks. In contrast, at SX-115, Na was significantly retarded relative to tracers (NO_3 and Tc), presumably due to the lower Na concentration in the SX-115 waste supernatant compared to SX-108 waste Supernate. Ca and Mg form very distinct peaks at the leading edge of the Na front under both tanks SX-108 and SX-115. Observations such as these, led Zachara (2001), Section D.3.1, to conduct a series of systematic adsorption experiments over a wide range of Cs and salt concentrations to develop an ion exchange model that could be used to predict Cs migration beneath the Hanford tank farms.

We report reactive transport experiments of Cs sorption to Hanford sediments, with the specific objective of testing the applicability of cation exchange models derived from batch experiments to calculate Cs mobility beneath the Hanford tank farms. These experiments couple Cs exchange thermodynamics determined for Hanford sediments based on the batch experiments (Zachara et al. 2001) and flow and transport using a reactive transport model (Steefel 2001). Our experiments included: (1) binary Na–Cs exchange experiments at two different high salt and Cs concentrations, (2) ternary K–Na–Cs exchange experiment, and (3) high base experiment in which mineral dissolution and precipitation affect Cs exchange. In addition to allowing the testing of the batch-derived exchange model, these experiments provide a more direct measure of Cs retardation in Hanford sediments, which can be used in field-scale analyses of transport (Sections D.3.7 and D.7.4). Our experiments investigated the reversibility of Cs exchange dominated by sorption to high affinity, frayed-edge sites on micas (FES sites), and to basal layers of expandable clay minerals such as smectite and vermiculite (clay sites). Results of the high salt reactive transport experiments form the basis for extending the cesium exchange model to reactive, hot tank wastes containing high base [OR].

D.3.3.2 Experimental and Modeling Procedures

D.3.3.2.1 Column Experiments. A total of 6 one-dimensional column experiments using uncontaminated Hanford sediments were carried out at 25 °C to investigate the reactive transport of Cs (Table D.3.3.1). The “Above B” Hanford formation composite (D.2.2, D.3.1.2.1) was used as the experimental medium. The sediment was lightly crushed to pass through a 2-mm sieve, air-dried, and mixed thoroughly. No further fractionation of the sediments was conducted. The sediments were loaded into a reactor column (1.06 cm x 15.27 cm) filled with distilled and deionized water. Sediment density was determined to be 2.67 g/cm³ by volume displacement. The reactive transport experiments consisted of three phases. In the pretreatment phase, the background electrolyte was passed through the column to replace K, Ca, and Mg with Na on the sediment exchange sites. Complete exchange was achieved in 7 to 10 pore volumes. The pretreatment phase of the experiment also provided an independent measure of the sediment cation exchange capacity (CEC). The pretreatment phase was followed by the Cs sorption experiment in which a CsI and NaNO₃ (or mixed KNO₃.NaNO₃, or NaOH) solution was passed through the sediment column to measure Cs retardation from the breakthrough curve. The final phase was a Cs desorption experiment in which the background electrolyte solution was passed through the sediment column to displace Cs from the exchange sites to assess the reversibility of the cation exchange reaction. Iodide behaved as a non-reactive tracer and was used to obtain a dispersivity of 1 cm. Aqueous samples exiting the column were analyzed for pH, Al, Ca, Cs, Fe, K, Mn, Mg, Na, and Si. The post-mortem sediments were examined by SEM/EDS and by X-ray diffraction for evidence of mineral reaction.

Table D.3.3.1. One-Dimensional Cesium-Reactive Transport Experiments.

Exp. No.	Inlet salt solution	Inlet Cs M	Flow rate (ml min ⁻¹)	Darcy flux (cm min ⁻¹)	Sediment: solution (g/L)	% Porosity
1	1 M NaNO ₃	10 ⁻⁴	0.1	0.025	3529.0	38.2
2	1 M NaNO ₃	10 ⁻⁴	0.02	0.113	3682.9	40.4
3	5 M NaNO ₃	10 ⁻⁴	0.1	0.121	3921.8	40.5
4	1 M NaOH	10 ⁻⁴	0.02	0.023	4195.1	38.9
5	1 M NaNO ₃	5 x 10 ⁻⁷	0.1	0.113	3818.1	41.1
6	0.1 M KNO ₃ 0.9 M NaNO ₃	10 ⁻⁴	0.1	0.113	3483.5	43.4

The sediment cation exchange capacity of the unreacted sediments were measured from triplicate ²²Na isotopic equilibrium experiments. Sodium saturated sediments were rinsed repeatedly with 2 mM NaNO₃ until a constant conductivity was reached to remove excess Na from the sediment pore water. The dry, treated sediments were then reacted in 2 mM NaNO₃ spiked with ²²Na (10⁵ dpm/ml ²²Na-NaNO₃) for 24 hours. After equilibration, the suspensions were centrifuged, and the supernatant was filtered and analyzed for ²²Na by liquid scintillation and total Na by ICP-AES. The sediment cation exchange capacity was also measured from the equivalent sum of Ca, K, Mg, and Na eluted with NaNO₃ and KNO₃ flushes of the sediments.

D.3.3.2.2 Modeling. Modeling of Cs transport in the column experiments was performed with the reactive transport code CRUNCH (Steefel 2001). The code includes the capability for simulating multi-component ion exchange coupled to aqueous complexation and mineral precipitation and dissolution. Two sets of input were used to carry out the reactive transport simulations. One set of selectivity coefficients and exchange site concentrations were determined from a global fit of all of the batch Cs-Na, Cs-K, and Cs-Ca exchange experiments (Zachara et al. 2001) at background electrolyte concentrations of 5 M or less (Figure D.3.3.1) (these are referred to as the “batch parameters”). The other set of selectivity coefficients and site concentrations was determined from batch and column experiments, with strong weighting of the column experiments in the optimization procedure (these are referred to as the “column parameters”). The fitting was carried out with the general fitting code PEST used in conjunction with speciation calculations carried out by CRUNCH. In this way, the resulting parameter set is fully compatible with the reactive transport simulations of Cs migration in both the column experiments and the field. The difference between the fits to the batch data presented here and those presented by (Zachara et al. 2001) is the inclusion of activity coefficient corrections and aqueous complexation in the fitting procedure presented here.

Figure D.3.3.1. Comparison of Cesium Exchange to Hanford Sediments Measure in Binary Batch Experiments (symbols) with Multi-Cation Exchange Model (solid lines) with Selectivity Coefficients and Exchange Sites Derived from a Global Fit to all of the Binary Data Shown in this Figure. Batch Data are from Zachara et al. (2001).

The selectivity coefficients in Table D.3.3.2 were fit assuming the Gapon activity convention:

where M is the exchanging cation (Na^+ , K^+ , Ca^{2+}) and m is its charge (Appelo and Postma 1996). The exchange reactions can then be used to write a standard mass action equation for binary Cs-M exchange:

$$K_{\text{M/Cs}} = \frac{[\text{M}_{1/m}\text{X}][\text{Cs}^+]}{[\text{CsX}][\text{M}]^{1/m}} \quad (\text{D.3.3.2.2})$$

Table D.3.3.2. Cesium Exchange Selectivity Coefficients, Ion Pair Formation Constants, and CEC Derived From a Global Fit to Zachara et al. [8] Batch Binary Exchange Experiments (Batch Parameters) and Derived From Fits Heavily Weighted with Column Exchange Experiments (Column Parameters).

Exchange reaction	Batch parameters Log K	Column parameters Log K
$\text{NaX1} + \text{Cs}^+ = \text{Na}^+ + \text{CsX1}$	6.96	6.85
$\text{NaX2} + \text{Cs}^+ = \text{Na}^+ + \text{CsX2}$	3.57	3.00
$\text{NaX3} + \text{Cs}^+ = \text{Na}^+ + \text{CsX3}$	1.64	2.10
$\text{KX1} + \text{Cs}^+ = \text{K}^+ + \text{CsX1}$	4.76	4.50
$\text{KX2} + \text{Cs}^+ = \text{K}^+ + \text{CsX2}$	1.44	3.77
$\text{KX3} + \text{Cs}^+ = \text{K}^+ + \text{CsX3}$	0.95	0.70
$\text{Ca}_{0.5}\text{X1} + \text{Cs}^+ = 0.5\text{Ca}^{2+} + \text{CsX1}$	7.53	7.13
$\text{Ca}_{0.5}\text{X2} + \text{Cs}^+ = 0.5\text{Ca}^{2+} + \text{CsX2}$	4.55	6.46
$\text{Ca}_{0.5}\text{X3} + \text{Cs}^+ = 0.5\text{Ca}^{2+} + \text{CsX3}$	1.44	1.58
$\text{NaNO}_3(\text{aq}) \rightarrow \text{Na}^+ + \text{NO}_3^-$	0.33	0.26
$\text{CsNO}_3(\text{aq}) \rightarrow \text{Cs}^+ + \text{NO}_3^-$	0.47	0.50
Bdot parameter (Cs-X)	1.66E-04	-8.90E-02
Exchange site	CEC ($\mu\text{eq g}^{-1}$)	CEC ($\mu\text{eq g}^{-1}$)
Site 1	0.027	0.037
Site 2	1.43	0.14
Site 3	86.6	102

Multiple exchange sites were needed to capture the large range in Cs- K_d as a function of Cs concentration. The need for multiple sites with differing affinities can also be seen by plotting conditional equilibrium constants as was done by (Zachara et al. 2001; Section D.3.1) who used a 2-site model to fit the data. Zachara et al. (2001) have presented the physical evidence for the

existence of at least two sites with very different affinities for Cs, one associated with the frayed edges of micas and the other with the surfaces of expansible layer silicates. We have fitted Cs exchange with a three-site model because it provides a substantially better fit of the Cs-Ca and, to a lesser extent, the Cs-Na exchange data. The three-site model was used because of the improvement it gave in matching the batch data—there is no clear physical evidence for more than two distinct sites actually present in the Hanford sediments. Detection of ^{137}Cs on mica minerals, but not on smectite minerals, from contaminated sediments beneath tank SX-108 (McKinley et al. 2001) may indicate that the very high Na concentrations estimated by Lichtner (Section D.7.3) in this tank leak suppressed Cs sorption to the basal sites on smectites, thereby leaving the frayed-edge sites on the micas as dominant Cs exchange mechanism. The observation from SX-108 sediments that Cs is associated almost exclusively with micas may not hold for other tank leaks where competing cation concentrations are lower than they are at tank SX-108.

We chose to fit the cation exchange capacity (CEC) rather than using an independently determined value, because there is significant uncertainty in the CEC determined for these Hanford sediments. The highest CEC value was determined by cation elution during preliminary washes of the sediment ($\text{CEC} = 99 \pm 13 \mu\text{eq/g}$) [this study]. The next highest CEC value was determined by extraction of K by NH_4 acetate ($\text{CEC} = 83 \mu\text{eq/g}$) [8]. The lowest CEC values were determined by ^{22}Na and ^{45}Ca isotopic equilibria measurements ($\text{CEC} = 46 \pm 3 \mu\text{eq/g}$) (Zachara et al. 2001, this study). Additional experiments are planned to help resolve the CEC so that it can be imposed as an independent constraint in the fitting of the exchange selectivity coefficients. The CEC of high affinity sites (as opposed to the total CEC) still needs to be fitted, however, since this cannot be determined with conventional CEC determinations. With the current model, the fits are non-unique as is shown by strong inverse correlation between selectivity coefficients for a particular site and the CEC of that site.

We used a standard Debye-Huckel formulation for activity coefficients augmented with fitting parameters for ion pair formation to describe solution activities accurately in the highly concentrated and variable Hanford system. Free cation activities were calculated by adjusting the log K_s for the ion pairs $\text{CsNO}_3(\text{aq})$, $\text{Ca}(\text{NO}_3)_2(\text{aq})$, and $\text{NaNO}_3(\text{aq})$ to match ion activities determined with the Pitzer approach as implemented in the code GMIN (Felmy 1995). In this respect, activity coefficients for the Debye-Huckel and Pitzer formulations do not match, but their ion activities do match. It was also necessary to include an empirical activity coefficient correction for the various Cs exchange species in order to capture the ionic strength dependence of the exchange. This took the form of a "Bdot" correction affecting only the activity of the exchange species:

$$\ln \gamma_{\text{Cs-X}} = BI \quad (\text{D.3.3.2.3})$$

D.3.3.3 Key Results

D.3.3.3.1 Dependence of K_d on Cesium and Competing Cation Concentration. The refitting of the batch data (Zachara et al. 2001) confirmed the strong variability of the Cs- K_d for Hanford sediments. The dependence of the Cs- K_d on the other cations (Na^+ , K^+ , and Ca^{2+}) is predicted by the ion exchange theory. We can rewrite Equation D.3.3.2.2 to obtain an expression for the dimensionless form of the distribution coefficient, K'_d :

$$K'_d = \frac{[CsX]}{[Cs^+]} = \frac{1}{K_{M/Cs}} \frac{[M_{1/m}X]}{[M]^{1/m}} \quad (D.3.3.3.1)$$

It follows that Cs retardation depends on the concentration of the competing ion because Cs retardation is described by:

$$R = 1 + K'_d = 1 + \frac{\rho_B K_d}{\phi} \quad (D.3.3.3.2)$$

where ρ_B is the bulk dry density of the sediment, and ϕ is the porosity. This is shown graphically by plotting the Cs- K_d versus Na concentration in solution (Figure D.3.3.2b). The Cs- K_d is also dependent on the Cs concentration in solution, because the different sites have different affinities for Cs exchange. If aqueous Cs concentrations are close to the concentration of the high affinity frayed-edge sites, then the retardation (or K_d) for Cs will be correspondingly high. However, if Cs concentrations significantly exceed the concentration of the frayed-edge sites, the K_d will be lower because Cs adsorption occurs on low affinity sites on the basal plane of expansible layer silicates. Figure D.3.3.2b shows the effect of Cs concentration on the Cs- K_d .

D.3.3.3.2 Multi-Cation Cesium Exchange Model—Batch-Derived Fits. Our results suggest that the Cs-Ca-Na-K exchange model derived from batch experiments predicts Cs retardation in Hanford sediments when Na or K concentrations are high enough to compete strongly for exchange sites. However, at lower Na and K concentrations, the model based on batch-fitted parameters underpredicts Cs retardation by 25 to 55 percent. In Figure D.3.3.3, we plot the model predictions and the experimental breakthrough curves of Cs. Retardation factors derived from the breakthrough data are summarized in Table D.3.3.3. In high salt solutions, 5 M NaNO₃, with relatively high Cs concentrations, 10⁻⁴ M, retardation is about 8 for both the model prediction and experiment. There is also a good match between model prediction and experiment in solutions containing K (0.1 M KNO₃, 0.9 M NaNO₃, and 10⁻⁴ M Cs), yielding a Cs retardation of about 12. However, in 1 M NaNO₃ solutions with no K, the model underpredicts Cs retardation at both high and low Cs concentrations. In the 1 M NaNO₃ experiments, Cs retardation is 41 at 10⁻⁴ M Cs and 282 at 5 × 10⁻⁷ M Cs, compared to predicted retardation equal to 26 and 226, respectively.

Table D.3.3.3. Comparison of Cesium Retardation Model.

Exp. No.	Inlet salt solution	Inlet Cs M	Observed retardation	Model retardation batch fit	Model retardation column fit
1	1 M NaNO ₃	10 ⁻⁴	42.9	26.9	36.7
2	1 M NaNO ₃	10 ⁻⁴	40.3	26.4	36.6
3	5 M NaNO ₃	10 ⁻⁴	7.6	8.0	7.1
4	1 M NaOH	10 ⁻⁴	38.7	32.4	42.5
5	1 M NaNO ₃	5 × 10 ⁻⁷	282.2	225.6	276
6	0.1 M KNO ₃ 0.9 M NaNO ₃	10 ⁻⁴	12.6	11.2	11.6

Figure D.3.3.2. The Dependence of Cs K_d on Dissolved Cs (A) and Sodium (B) Concentrations Calculated with the Multi-Cation Exchange Model.

Figure D.3.3.3. Cesium Reactive Transport Through Hanford Sediments in NaNO_3 and Mixed $(\text{K}, \text{Na})\text{NO}_3$ Solutions.

Note: Comparison of cesium breakthrough curves predicted by the multi-cation exchange model derived from batch experiments (lines) with experiments (symbols).

The variable agreement between the model predictions and experiments appears to be partly an artifact of fitting the batch data on a logarithmic scale. Our fits to the batch data on a log-log plot are visually very close (with the exception of 0.01 M Cs-Na exchange), with discrepancies on the order of 0.1 log unit or less. The global fit of the batch data slightly underpredicts exchange in the 1 M NaNO₃ batch experiments and slightly overpredicts exchange in the 5 M case. Although these discrepancies are small in log space, they translate into significant differences in the prediction of the total mass of exchange Cs and the resulting retardation in the column experiments. We evaluated this effect by weighting the batch exchange experiments at the NaNO₃ concentration corresponding to the conditions of the column experiment (Table D.3.3.4). Weighting the data in this fashion improves the match between the observed and calculated retardation, but it does completely eliminate the discrepancies. Additionally, this approach limits the global application of the ion exchange model over a wide range of solution compositions that are required to model Cs migration beneath the Hanford tanks.

Table D.3.3.4. Observed versus Calculated Retardation of Cesium for Case: Slowly Reversible Sites are Included in the Batch Fit Optimized for 1 M Salt Concentrations

Exp. No	Inlet salt solution	Observed retardation	Model retardation.	Model retardation ^b
1	1 M NaNO ₃	428	34.3	
2	1 M NaNO ₃	40.3	35.5	40.5
3	5 M NaNO ₃	7.6	83	
5	1 M NaNO ₃	282	230	262
6	0.1 M KNO ₃ 0.9 M NaNO ₃	126	11.3	

D.3.3.3.3 Multi-Cation Cesium Exchange Model—Column-Weighted Parameters.

To further evaluate the ion exchange model, we modify our Cs-Na-K-Ca exchange model by fitting the selectivity coefficients and the cation exchange capacity with weighted results from our column experiments (Figure D.3.3.4 and Table D.3.3.2). Batch experiments are included in the fitting procedure because the column experiments do not cover the entire range of cation concentrations. The inclusion of the column-weighted data improves the match between predicted and observed Cs retardation in the 5 M NaNO₃, 1 M NaNO₃, and the mixed 0.1 M KNO₃ and 0.9 M NaNO₃ experiments. There are two significant differences between the model parameters fitted with the batch data and those fitted with the column data. One is the increase in the concentration of site 3 from 88.6 to 102 µeq/g. A second difference is the higher affinity for Cs over Na on site 3 where the log K increases from 1.64 to 2.10. Both of these predict a higher overall mass of Cs on exchange sites for a given aqueous concentration of Cs and thus higher Cs retardation. Changes in the selectivity coefficients for the Cs-K and Cs-Ca exchange reactions are directly linked to the higher CEC in the column-derived parameters. This reflects the non-uniqueness of the model, since the column experiments (102 µeq/g) provided no new data for the Cs-K-Ca systems (in the experiment containing K, the experiment agreed with the

model prediction based on the batch data). The higher CEC determined from a fit of the column experiments ($102 \mu\text{eq/g}$) is supported by the CEC estimated from the pretreatment phase of the column experiments (Figure D.3.3.5). The equivalent concentrations of eluted K, Ca, Mg, and Na in the pretreatment phase using 1 M NaNO_3 and 1 M KNO_3 in multiple column experiments equals $99 \pm 13 \mu\text{eq/g}$. However, caution must be used in interpreting results based on the CEC alone because of the non-uniqueness of the fitting parameters—it is the combination of fitted CEC and selectivity coefficients that determine the predicted cesium retardation. It is doubtful that soluble salts contribute to an erroneously large CEC, because cation concentrations measured in sediments in contact with distilled waters are quite small.

D.3.3.3.4 Cesium Exchange to Frayed-Edge Sites on Micas and to Basal Layers of Expansible Layer Silicates. We have tested the Cs exchange model in the Cs-Na binary system at two different initial Cs concentrations (5×10^{-7} and 10^{-4} M) and two different salt concentrations (1 and 5 M NaNO_3). These two Cs concentrations were selected to test the ability of the model to predict Cs mobility where retardation is dominated by exchange to the less abundant, high affinity, frayed-edge sites on micas (5×10^{-7} M) and by sorption to the abundant, lower affinity exchange sites on expansible layer silicates (10^{-4} M) (Figure D.3.3.4). We find good agreement between the revised model predictions and the experiment for Cs retardation (Figure D.3.3.4), indicating that this model may be applied over the range of Cs and salt concentrations present in WMA S-SX tank wastes leaking into the vadose zone sediments.

D.3.3.3.5 The Effect of Potassium on Cesium Exchange in High Salt Solutions. Potassium will enhance the mobility of Cs because it has a higher affinity for the exchange sites on micas and clays than does either Na or Ca. Our multi-cation exchange model predicts that in solutions with equal concentrations of K and Cs, K will displace about 10% of the Cs on the exchange sites (batch parameters, Table D.3.3.3). Since the tank wastes contain elevated concentrations of K as well as in Na (Section D.7.3), we conducted exchange experiments in the K-Cs-Na system to further test the ion exchange model. Another source of K in the contaminant plume is from the dissolution of mica and feldspar minerals in the highly alkaline and thermally hot waste stream. Validation and improvement of the ion exchange model with ternary K-Cs-Na experiments at neutral pH are needed before it can be realistically applied to high-base experiments.

Figure D.3.3.4 compares the column transport behavior of Cs in binary (Cs-Na) and ternary (K-Cs-Na) electrolyte systems. The initial Cs concentration (10^{-4} M) and total salt concentration (1 M) are the same in both experiments. In salt solutions containing 0.1 M KNO_3 and 0.9 M NaNO_3 Cs retardation is one-third of its retardation in 1 M NaNO_3 . We see excellent agreement between the predicted breakthrough and the experimental breakthrough.

D.3.3.3.6 Cesium Exchange in High-Base Solutions. It is important to establish whether the multi-cation Cs exchange model can be extrapolated to the high-base concentrations reported to exist in the S and SX tank farms waste (Section D.7.3). While pH does not have a direct effect on Cs exchange, it can have an indirect effect through aqueous complexation or mineral dissolution. In the nitrate-dominated system considered here, the pH dependence of complexation is minimal (although there is some complexation as CsOH_{aq} and NaOH_{aq}). Mineral dissolution and precipitation reactions can affect Cs mobility by altering the number and distribution of sites and by providing a source for dissolved K that competes for Cs exchange.

Figure D.3.3.4. Cesium Reactive Transport Through Hanford Sediments in NaNO_3 and Mixed $(\text{K},\text{Na})\text{NO}_3$ Solutions.
Comparison of Cesium Breakthrough Curves Predicted by the Multi-Cation Exchange Model Derived from
Fits Weighted to the Column Experiments (lines) with Experiments (symbols).

Figure D.3.3.5. The Cation Exchange Capacity Measured From the Equivalent Concentration of Ca, K, Mg, Exchanged for Na in 1 M NaNO₃ Flushes of the Sediment Column, and Na Exchange for K in 1 M KNO₃ Flushes of the Sediment Column,

Note: The NaNO₃ and KNO₃ flushes were conducted in separate experiments with fresh sediments.

Figure D.3.3.6 compares Cs breakthrough curves and associated model predictions from the 1 M NaOH experiment (pH 13.7) and the 1 M NaNO₃ experiments (pH 8) both with Cs = 10⁻⁶ M. Cs retardation was underpredicted in the 1 M NaNO₃ experiments and overpredicted in the 1 M NaOH experiments by about the same amount (10 to 15%). This suggests that the model can be extended to the alkaline tank waste, because the reactive transport behavior of Cs was not significantly affected by the presence of base and the associated mineral alteration. The model used in Figure D.3.3.6 incorporated the measured OH⁻ and K⁺ (1.5 × 10⁻⁴ M) at steady-state, but did not explicitly account for mineral dissolution or precipitation. About 4 wt% of the sediment dissolved based on the composition of the output solutions. During the first few hours of reaction there was rapid mineral dissolution and re-precipitation in the sediments. SEM and EDS analyses of the sediments at the end of the experiment revealed a precipitate that was rich in silica, Fe, Mg, and Ca. This precipitate is probably amorphous, because it was not detected by XRD (Personal Communication, D. Bish, LANL). The concentration of dissolved K in the high base experiments (1.5 × 10⁻⁴ M) had a small but detectable effect, lowering slightly the Cs retardation. Enhanced retardation in the 1 M NaOH experiments compared with the 1 M NaNO₃ experiments is consistent with the moderate increases in CEC reported in base-treated sediments in Section D.3.1.

Figure D.3.3.6. Comparison of Cesium Reactive Transport Through Hanford Sediments in 1 M NaNO₃ and 1 M NaOH Solutions.

Note: Cesium breakthrough curves predicted by the multi-cation exchange model derived from fits weighted to the Column Experiments are shown by lines. The experimental data is shown by symbols.

D.3.3.3.7 Reversibility of Cesium Exchange. The Cs exchange model presented here assumed Cs exchange to the frayed-edge mica sites and to basal clay surfaces was rapid and reversible. It does not consider the impacts of poorly reversible Cs exchange. Laboratory studies show that Cs may diffuse within mica microfissure, interlamellar, and collapsed frayed-edge sites effectively fixing the Cs to the solids (Lomenick and Tamura 1965; Klobe and Gast 1970; Le Roux et al. 1970; Comans et al. 1991; Smith and Comans 1996). Preliminary measurements of Cs desorption from contaminated WAM S-SX sediments (41-09-39 and SX-108) indicate partial fixation of the sorbed Cs pool (McKinley et al. 2001). It is important to assess the reversibility of Cs exchange as a basis for predicting future mobility.

Figure D.3.3.7 shows Cs breakthrough and desorption for three experiments, 10^{-4} M Cs and 5 M NaNO_3 , 5×10^{-7} M Cs and 1 M NaNO_3 , and 10^{-4} M Cs and 1 M NaOH, as well as their respective model predictions based on the column parameters. In our reactive transport experiments, Cs exchange is fully reversible only in experiments where Cs and competing salt concentrations are high. In the 10^{-4} M Cs and 5 M NaNO_3 experiment, 98% of the sorbed Cs was desorbed when flushed with 5 M NaNO_3 . Under these conditions, Cs sorption was dominated by exchange to basal sites on the expandable clays. At lower Cs and salt concentrations, however, Cs sorption was dominated by exchange at high affinity, frayed-edge mica sites. In the experiment using 5×10^{-7} M Cs and 1 M NaNO_3 , about 70% of the sorbed Cs was desorbed by 1 M NaNO_3 . As indicated by equilibrium modeling, most of the residual sorbed Cs remains there because of the high site affinity, not because of irreversible behavior. Because of the high binding affinity of the frayed-edge sites, many pore volumes are required to completely remove Cs. However, there was some evidence for irreversibility as indicated by the discrepancy between the equilibrium modeling results and the observed Cs concentrations during desorption. This is best shown in Figure D.3.3.7b. During the sorption phase (282 to 617 pore volumes), the lower Cs concentrations in the effluent compared to the model results may indicate that some Cs is incorporated in poorly reversible exchange complexes. Similarly, during the desorption phase, the observed Cs concentrations are higher than those predicted by the equilibrium modeling, indicating slow Cs desorption.

Figure D.3.3.7. Reversibility of Cs Exchange when Flushing the Sediments with 5 M NaNO₃ (A), 1 M NaNO₃ (B) and 1 M NaOH (C) Solutions at the End of the Sorption Experiments. Experimental Data are Shown with the Symbols. Model Predictions are Shown with the Lines.

In the high base experiment using 1 M NaOH and 10^{-4} M Cs, most of the Cs sorption should occur on reversible, low affinity sites. However, only about 72% of the Cs was desorbed by 1 M NaOH (Figure D.3.3.7c). Unlike the 5×10^{-7} M and 1 M NaNO₃ experiment (Figure D.3.3.7b), which exhibited a constant release of Cs during the last half of the experiment, the release of Cs approached zero in the outflow solution of the 1 M NaOH experiment. The relatively large amount of Cs that did not desorb (28%) indicates Cs immobilization due to alteration of the sediments by base reaction. These results are consistent with exchange experiments conducted with contaminated sediments (41-09-39 and SX-108) which showed higher release of Cs when the sediments were treated with an NH₄-acetate extraction (Section D.3.6).

The discrepancy between the equilibrium modeling and observed results was used to assess the concentration of slowly reversible exchange sites. During the sorption stage between 282 and 617 pore volumes, the discrepancy between the model and the results indicated the sorption of 7.5×10^{-6} moles total Cs to slowly reversible sites. On the desorption limb, the discrepancy corresponded to 9.5×10^{-6} moles total Cs. In Experiment 2, carried out with 10^{-4} M Cs, the discrepancy during the sorption phase corresponded to 4×10^{-4} moles total Cs. These masses of Cs associated with the slowly reversible sites were minimum values, since their concentrations are not easily discovered from the breakthrough of Cs.

We have established that a discrepancy exists between the batch-based ion exchange model and the experimental column data. In this analysis we have applied “corrections” for sorption to the slowly reversible sites (Table D.3.3.4). Using the discrepancy between the equilibrium model and the observed results for the 5×10^{-7} M Cs and 1 M NaNO₃ experiment (Experiment 5), we calculated an average rate of Cs sorption to these sites of 4.9×10^{-8} mol/hr from 282 to 617 pore volumes. The application of this rate of Cs incorporation into the slowly reversible sites increased the predicted breakthrough from 230 to about 262 pore volumes. This retardation value is within 7% the experimentally observed retardation of 282 pore volumes (Table D.3.3.4). We applied the same analysis to Experiment 2 where the aqueous Cs concentration was higher, 10^{-4} M Cs. In this case, we calculated an average rate of Cs exchange at these sites equal to 1.3×10^{-5} mol/hour. When this “correction” was applied, the predicted retardation shifts to about 40.5, in agreement with the experimental value (Table D.3.3.4). Note that this interpretation of the batch-column discrepancy relies on a kinetic chemical process as opposed to diffusion-controlled transport into immobile zones within the sediment. A rate-limited process based on diffusion through porous media would have no effect in a batch system where stirring makes the sediment material fully accessible to the bulk solution.

Additional evidence for slowly reversible Cs exchange was observed in column experiments with 10^{-4} M Cs and 1 M NaNO₃ run at two different flow rates (Figure D.3.3.6a). In Experiment 1 (see Table D.3.3.1) run at 0.02 ml/min, the retardation of Cs was slightly greater ($R = 43$) than that observed in Experiment 2 run at 0.1 ml/min ($R = 40$). The higher retardation may have resulted from the longer time available for Cs sorption to slowly reversible sites. Note also that Experiment 1 (which was run at a slower flow rate and over a longer period of time than Experiment 2) showed slightly better agreement with the equilibrium reactive transport model than did Experiment 2. Finally, Experiment 5, which was designed to increase the relative importance of the FES versus clay sites by using a lower Cs concentration, showed the strongest kinetic effects.

D.3.3.4 Conclusions and Implications

One of the most significant implications of this work is the confirmation that the ^{137}Cs distribution coefficient is not constant over the range of Na, K, Ca, and Cs concentrations found in the tank farm inventory and in the vadose zone pore water at the S and SX tank farms. Vadose zone processes, such as dilution from infiltrating rainwater (or water leaking from pipes) or concentration from boiling waste, will dramatically alter the ^{137}Cs K_d over time and space. Moreover, a ^{137}Cs K_d determined directly from the contaminated sediments is suspect unless proper adjustments are made, because those determinations typically involve dilutions as part of the analytical procedure. A 10x dilution, for example, could easily result in overestimating the K_d by a factor of 3 to 10. Similar cautions apply even when no dilutions for analytical purposes are carried out, because infiltration of rainwater in the vadose zone is likely to have diluted cation concentrations from what they were at the time of the leak. It is quite probable that a K_d determined from present day contaminated sediments might significantly overestimate the Cs retardation at the time of the tank leaks.

The multi-cation exchange model captures much of the chemical effects responsible for the dependence of ^{137}Cs K_d on competing cation and Cs concentrations and is a significant improvement over the use of a constant K_d to model ^{137}Cs from tank leaks to the vadose zone sediments. However, there is some mismatch between the predictions derived from a global fit of batch data covering a wide range of Cs and salt concentrations and our 1-D column experiments. Part of the mismatch appears to be related to the sorption of Cs at slowly reversible sites, which has not yet been included in the modeling except in an empirical sense (e.g., Table D.3.3.4). Additional experimental data is needed to better quantify these sites. In the absence of new experimental data, model parameters based on weighted column experiments can be used in field-scale analyses of transport to provide a more direct measure of retardation of Cs Hanford sediments (Sections D.3.7 and D.7.4).

The following example shows that the multi-cation exchange model describes ^{137}Cs retardation that is consistent with ^{137}Cs observations at the SX tank farm. Our column experiments indicate that high competing cation concentrations associated either with the tank liquors or resulting from reactions in the sediment underlying the tank cause a significant decrease in the retardation of Cs. The tank SX-115 leak apparently contained about 3.5 M NaNO_3 and 8×10^{-5} M Cs. Our model for Cs migration suggests a dimensionless Cs K_d of about 10 prior to any dilution of the tank liquors by vadose zone processes. This qualitatively agrees with the strong retardation of Cs observed below tank SX-115. In addition, some retardation of Na is expected upon dilution of the leaked waste, again in agreement with observations made in borehole WB 23-19 (Seme et al. 2001a, b). In contrast, leaking tank liquors at SX tank farm was at or above the boiling temperature and was extremely concentrated, with some estimates giving NaNO_3 concentrations at or close to equilibrium with respect to solid NaNO_3 (about 19.5 molal at 100°C; Section D.7.3) and 7×10^{-4} M Cs. At these very high NaNO_3 concentrations, one does not expect to see any retardation of Na, in agreement with field observations that show Na peaks are coincident with nitrate peaks. One also expects significantly less retardation of Cs as well. Extrapolating the column-weighted fits of Cs exchange to 15 M yields a predicted Cs retardation of between 2 and 3. This value is close to the observed retardation below tank SX-108 of 2.5 to 3 (Seme et al. 2001a, b). While this prediction is uncertain until we have direct experimental Confirmation of Cs retardation at these NaNO_3 concentrations and at higher temperature, the ion exchange model

presented here suggests that the high salt concentrations account for the bulk of the enhanced Cs mobility observed, particularly below tank SX-108.

An important aspect of the present study has been to provide additional scientific justification for the ion exchange model proposed by (Zachara et al. 2001) to describe Cs migration in Hanford sediments. We believe the combination of reactive transport modeling and column flow-through experiments provide very strong support for the applicability of the ion exchange model. As summarized above, our results suggest that the bulk of the enhanced migration of Cs observed below tanks like tank SX-108 is the result of the very high salt concentrations in these tanks. Tanks with lower salt concentrations than tank SX-108 show correspondingly higher Cs retardation. The multi-site ion exchange model also indicated that relatively dilute fluids of the kind associated with natural infiltration are unlikely to mobilize Cs in the subsurface. The ion exchange model, however, does suggest that considerable caution should be used in designing any sluicing methods, since re-injection of a concentrated sluicing solution is likely to result in further Cs migration.

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D.3.4 CS⁺ TRANSPORT IN UNSATURATED SEDIMENTS FROM THE S AND SX TANK FARMS

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D.3.4.1 Introduction

Regions of stagnant or immobile water develop in unsaturated sediments (Nielsen and Biggar 1961; Biggar and Nielsen 1962; Gaudet et al. 1977; Bond and Wierenga 1990). Immobile water may exist in *thin* liquid films around soil particles, in dead-end pores, or as relatively isolated regions associated with unsaturated flow (Nielsen et al. 1986). Mass transfer in and out of the immobile water domain is diffusion-limited; advective transport is restricted to the mobile water domain. A two-region transport model is used to describe this hydrodynamic condition.

Recent research on Hanford sediments illustrates an increase in the fraction of immobile water with decreasing water content (Gamerdinger and Kaplan 2000). Retardation due to sorption during unsaturated transport has not been widely investigated in systems with a significant fraction of immobile water. Uranium (U[VI]) transport in unsaturated sediments at higher water contents (greater than 50% moisture saturation) was generally predicted from sorption and transport that was determined in saturated systems (Gamerdinger et al. 2001a, b). This corresponded to conditions where transport was described with a single flow domain (all water present in the mobile domain). At lower water contents (less than 30% moisture saturation), retardation was less than predicted from sorption parameters that were determined in saturated systems (Gamerdinger et al. 2001b). This corresponded to conditions where a significant fraction of the water was present in the immobile water domain.

The above observations were made in systems where the solute was introduced to the sediment column during transport. There are two related mechanisms to explain changes in sorption during transport that are not predicted from measurements in saturated systems, and changes that are only apparent in systems with a significant fraction of immobile water. One is rate-limited mass transfer of the solute to sorption sites that are associated with the immobile water domain.

The significance of rate-limited mass transfer is determined by the average pore water velocity and the fraction of water in the immobile domain. The velocity of the solute in the mobile domain increases in proportion to the fraction water in the immobile water domain. For example, if the fraction of water in the mobile domain is 0.2, the velocity of solutes in the mobile domain increases by a factor of 5 relative to the average pore water velocity. Solutes moving through the mobile domain at the faster velocity have diffusion-limited access to sorption sites that are associated with the immobile water domain. Previous research with U(VI) indicated decreased sorption with increasing velocity; the changes with velocity at several moisture contents were consistent with the rate-limited mass transfer mechanism (Gamerdinger et al. 2001a).

The other possible mechanism to explain decreased sorption under conditions where a significant fraction of the water is present in the immobile water domain is a complete loss of access to

sorption sites in the immobile water domain. This contrasts diffusion-limited access, described above. If pore water in the immobile water domain is physically disconnected from the mobile domain, solutes that enter the system through the mobile domain do not have access to sorption sites in the immobile water domain. These solutes would appear to be excluded from a fraction of the pore volume. This mechanism has been suggested in research on U(VI) transport in unsaturated coarse- and fine-textured sandy sediments at moisture contents equivalent to 14 and 22% moisture saturation, respectively (Gamerding et al. 2001b). To date, this phenomenon has only been demonstrated in coarse-textured sandy sediments.

The objective of this research was to investigate Cs^+ transport in unsaturated sediments under geochemical conditions analogous to the water saturated column experiments discussed in Section D.3.3. Retardation under hydrodynamic conditions where a significant fraction of water was associated with an immobile water domain was of particular interest as these conditions are implied by the low moisture contents recorded in sediments from the SX-108 core. One goal was to determine whether Cs^+ transport at low unsaturated water contents (less than 30% moisture saturation) was predictable from batch and column measurements performed under saturated moisture conditions.

D.3.4.2 Experimental Procedures

D.3.4.2.1 Materials and Methods. The materials and geochemical conditions were selected to be consistent with previous (Zachara et al. 2001) and ongoing investigations of Cs^+ sorption in Hanford sediments (Sections D.3.1 and D.3.3). The less than 2 mm size fraction of the air-dried “Above B” composite sediment (D.2.2) was used without additional treatment. The aqueous solution for all experiments was 5 M NaNO_3 . Solutions of 5.4×10^{-5} M Cs^+ were prepared by dissolving CsI in 5 M NaNO_3 . Pentafluorobenzoic acid (PFBA) was used as a conservative, non-sorbing tracer in separate experiments to assess hydrodynamic conditions. Cs^+ concentrations were determined by ICP-MS; PFBA concentrations were determined by HPLC with UV detection at 254 nm.

D.3.4.2.2 Transport Experiments in Re-Packed, Unsaturated Columns. Retardation during transport in unsaturated sediments was determined using a centrifuge method; the experimental system and method are described in detail elsewhere (Gamerding and Kaplan 2000). A brief description of the approach follows and is similar to that used for saturated column (miscible displacement) experiments (Section D.3.3). Columns (length, $L = 6.0$ cm, radius, $r = 2.25$ cm, bulk volume, $V_{\text{bulk}}, 95.43 \text{ cm}^3$) had mesh at the inflow and outflow; the outflow was lined with grade 230 filter paper (Whatman, Inc., Clifton, New Jersey). Columns were packed with the “Above B” composite sediment and were completely saturated with NaNO_3 solution. Sediment bulk density, ρ (g/cm^3), and volumetric water content, θ (cm^3/cm^3), were determined from the mass of the sediment and/or water. The percent moisture saturation was calculated from the ratio of θ (water-filled porosity), to the total porosity, ϕ , which was calculated from the bulk density and an assumed particle density of $2.65 \text{ g}/\text{cm}^3$.

With the centrifuge method (Model L8-UFA, Beckman Coulter, Inc., Fullerton, CA), water content is influenced by centrifugal force and the fluid flux, q (cm/hr), which was controlled with a volumetric infusion pump (AVI 210A, 3M, St. Paul, Minnesota). Columns were first saturated by passing four saturated pore volumes through the column; columns were then placed in the

centrifuge. A pore volume is defined as the volume of water within the porous media at a particular water content. Additional NaNO_3 was passed through the column during equilibration to attain steady-state conditions. Unsaturated transport experiments were initiated when the columns had reached a steady-state, average water content. Experiments at the different water content and velocity conditions were executed consecutively on the same column. Cs^+ and PFBA were applied as step inputs (separate experiments) where the pulse length, t_o , is defined as the volume of the step input, expressed as the number of column pore volumes. Practical considerations resulted in variation of t_o . Effluent was collected manually and analyzed for Cs^+ or PFBA. For each effluent sampling, rotation of the centrifuge and flow were stopped. Prior evaluation indicates no significant effect of stopping flow on the transport of non-retarded, conservative solute tracers (Gamerding and Kaplan 2000). The stop-flow interval provided additional time for rate-limited mass transfer of U(VI) , however; the effect on retardation was dependent on the length of the stop-flow interval relative to the average pore water velocity (i.e., greater impact for faster velocity experiments).

D.3.4.3 Results

Results of transport experiments are expressed as breakthrough curves (Figures D.3.4.1 to D.3.4.3). The measured parameters that define the experimental conditions, and parameters determined from the breakthrough curves, are listed in Table D.3.4.1. They are defined as introduced in the text and are summarized as footnotes in Table D.3.4.1. The experiments are identified by the prefix of “CC” for Cs^+ , and “CP,” for PFBA, followed by the percent moisture saturation. For example, CC-26 represents a Cs^+ transport experiment at 26% moisture saturation. Percent moisture saturation is defined as the percent of the total porosity that is water-filled. The percent recovery of the analyte in the effluent was based on the area under the BTC compared with the measured step input. The retardation factor, R , is defined as the average velocity of water relative to that of the solute. R values are based on the center-of-mass and were determined from the mathematical first moment (Valocchi 1985).

D.3.4.3.1 Conservative Tracer Transport and Hydrodynamic Properties. Results of the tracer experiments are presented in Figure D.3.4.1 and Table D.3.4.1. Recovery was 98% at both water contents (CP-65, CP-28). Retardation factors were approximately one and indicate solute transport at the velocity of water. R values less than 1 suggest exclusion of the solute from a fraction of the water-filled pore volume. The exclusion phenomenon that was observed previously in unsaturated coarse- and fine-textured sandy sediments from Hanford (Gamerding et al. 2001b) was not observed for the “Above B” composite sediment at 28% moisture saturation (CP-28). Complete particle size characterization (sand, silt, clay) was not available; however, the composite sediment appeared to contain a greater fraction of silt-sized particles than the coarse and fine sands. Because of the sediment texture, water content, and hydrodynamic condition (solute exclusion not observed), the “Above B” composite sediment was not suitable for evaluating the phenomenon of “disconnected” pore water. When this occurs, solutes are excluded from a fraction of the pore volume and, therefore, sorption sites associated with a portion of the immobile water domain. This exclusion phenomenon has been demonstrated in sand-textured sediments and results in accelerated transport due to decreased sorption: solutes in the mobile domain do not have access to sorption sites that are associated with disconnected pore water. Because there is a significant fraction of immobile water at less than or equal to 28% saturation, the “Above B” composite sediment is suitable for evaluating diffusion-limited access to sorption sites in the immobile water domain.

Table D.3.4.1. Measured and Calculated Parameters for PFBA and Cs⁺ Transport Experiments on the "Above B" Composite Sediment.

Expt.	Analyte	Sat. (%)	F (cm ³ hr ⁻¹)	ρ_b (g cm ⁻³)	θ (st. dev.)	V _w (mL)	V (cm hr ⁻¹)	t ₀ (V _w)	Re veD (%)	R	P	β	ω
CP-65	PFBA	65.3	74.4	1.609	0.256 (0.004)	24.47	18.24	2.91	98	1.05	18	-	-
CP-28	PFBA	27.6	33.0	1.609	0.109 (0.001)	10.36	19.11	3.17	98	1.05	9	0.182	1.24
CC-66	Cs ⁺	65.6	74.4	1.609	0.258 (0.001)	24.61	18.14	29.26	97	11.6	18	-	-
CC-26	Cs ⁺	25.8	33.0	1.609	0.101 (0.007)	9.68	20.44	45.97	92	13.2	9	0.183	1.24
CC-23	Cs ⁺	22.8	6.9	1.609	0.089 (0.003)	8.54	4.85	25.47	74	24.1	9	0.182	1.24

^aF = flow rate; ρ_b = bulk density; θ = average volumetric water content (standard deviation); V_w = average pore volume; v = average pore water velocity; t₀ = step input; R = retardation factor.

Figure D.3.4.1. Conservative Tracer (pentafluorobenzoic acid) Transport Through the “Above B” Composite Sediment at Two Moisture Contents.

Note: Transport at 65% saturation is consistent with a one-region flow domain and is described with the convection-dispersion-transport equation (CDE). At 27.6% saturation, the left-shift and tailing suggest mobile-immobile water, requiring a two-region transport model.

Hydrodynamic parameters were determined from the breakthrough curves (BTCs) of the tracers. At 65% moisture saturation (CP-65), the conventional single-flow domain form of the convection-dispersion equation, CDE, was adequate for characterizing the BTC. The dimensionless Peclet number, P , which includes hydrodynamic dispersion, D ($P = vL/D$, where v is the average pore water velocity), was determined by a single-parameter curve fit.

At 28% moisture saturation (CP-28), the conventional CDE failed to capture the early breakthrough and tailing phenomena that is characteristic of mobile-immobile water (Figure D.3.4.1); a two-region model was applied to describe the BTC. The criteria for using a two-region model is when the Peclet number determined with the CDE is less than 2, and the fraction immobile water determined with the two-region model is greater than 10% (Gamerding and Kaplan 2000). The dimensionless parameters, β and ω , were determined by curve-fitting. β defines the fraction of mobile water, subscript m , ($\beta = \theta_m/\theta$, where θ is the volumetric water content); ω is the dimensionless coefficient for mass transfer between mobile and immobile water domains ($\omega = \alpha L/q$, where α is the mass transfer coefficient (1/hr), L is the column length, and q is the water flux). For these cases, the Peclet number, P , was calculated directly from the slope of the BTC where c/c_0 was equal to 0.5 (Gamerding and Kaplan 2000).

Hydrodynamic parameters (P , β , ω) are presented in Table D.3.4.1. As anticipated, hydrodynamic dispersion and the fraction of immobile water increase with decreasing water content. Nearly 82% of the water in the sediment at 28% saturation is associated with the immobile domain (Table D.3.4.1, CP-28, $\beta = 0.182$). Although the average pore water velocity was controlled across experiments (Table D.3.4.1, range of 18.1 to 20.4 cm/hr), it is important to

recognize that advective transport is limited to the mobile domain, and the velocity of solute in the mobile domain ($v_p = v / \phi_m$) at 28% moisture saturation (CP-28) is 105 cm/hr, which is quite rapid.

D.3.4.3.2 Cs⁺ Transport and Retardation. Cs⁺ transport at 66 and 26% moisture saturation is illustrated in Figure D.3.4.2 (CC-66 and CC-26, Table D.3.4.1). The BTCs indicate that a small fraction of the Cs⁺ continued to elute from the column when the experiments were terminated (recovery was 97 and 92% for CC-66 and CC-26, respectively). This suggests that a fraction of the sorption is less reversible, as shown by Zachara et al. (2001).

Cs⁺ retardation during transport in unsaturated columns was determined and compared with predictions that were based on retardation in saturated columns (LLNL; Section D.3.3). The approach used here is limited to the use of readily available transport models and parameters that could be determined from the retardation factor (e.g., a bulk, equilibrium distribution coefficient, or K_d value). The retardation factor that was determined for saturated conditions ($R=7$) was used to determine a K_d value. The K_d value was then used to estimate expected retardation for transport experiments at lower water contents. This approach accounts for changes in retardation that are expected due to the change in the soil:water or mass:volume ratio. Isotherm nonlinearity is recognized and will be incorporated in subsequent modeling of Cs⁺ transport.

Cs⁺ transport at 66% moisture saturation is shown in Figure D.3.4.2A. The observed retardation ($R = 11.6$, Table D.3.4.1) agrees well with the independent prediction that was based on retardation determined in a saturated column ($R = 10.5$). The model prediction assumes a linear isotherm and does not account for nonlinear sorption behavior, which is known to be significant for Cs⁺. Isotherm nonlinearity contributes to the asymmetry that is apparent in the observed breakthrough curve.

Cs⁺ transport at 26% moisture saturation is shown in Figure D.3.4.2B. As discussed for the conservative tracer, the early breakthrough on the front and prolonged tailing on the back of the BTC are indicative of rate-limited mass transfer. The observed retardation ($R = 13.2$, Table D.3.4.1) is almost a factor of 2 lower than predicted from retardation in the saturated column ($R = 25.2$). Under-estimation of Cs⁺ transport is illustrated by independent model predictions with $R = 25.2$ using both one-region (conventional CDE) and two-region transport models. Hydrodynamic parameters for the two-region model were determined from conservative tracer data. A semi-independent prediction with the two-region model and R equal to the observed value of 13.2 also failed to capture the observed transport behavior. This is likely because the model does not account for isotherm nonlinearity.

Even though the *average* pore-water velocity was consistent for the three moisture contents (100%, 66%, and 26% saturation), at 26% saturation the velocity of the solute in the mobile domain is accelerated by a factor of 5 (80% of the pore water is associated with the immobile water domain). This illustrates how a significant fraction of immobile water accelerates solute transport and decreases sorption because of diffusion-limited access to sorption sites associated with the immobile water domain. If all of the pore space is accessible by diffusion (as indicated by conservative tracer data), reducing the pore water velocity should result in increased sorption. This was evaluated with an additional experiment at a slower pore water velocity.

Figure D.3.4.2. Cs^+ Transport Through the "Above B" Composite Sediment at 66% (A) and 26% (B) Moisture Saturation:

Note: **A.** Transport at 66% saturation is predicted from retardation in saturated columns and is described with the convection-dispersion transport equation (CDE). **B.** Retardation at 26% saturation is not predicted from saturated columns ($R = 25.2$); Transport is faster by a factor of 2. Even when accounting for the hydrodynamic effect of mobile-immobilewater ($R = 13.2$, Two-Region), the breakthrough curve is not well described, likely because the model does not account for isotherm nonlinearity.

Cs^+ transport at 23% moisture saturation and a reduced pore water velocity of 4.85 cm/hr is shown in Figure D.3.4.3. The observed retardation (CC-23, $R = 24.1$, Table D.3.4.1) is somewhat less than predicted by Cs^+ transport in a saturated column (predicted $R = 30.3$); however, the experiment was terminated early due to mechanical problems and recovery was only 74%. This demonstrates increased retardation due to a reduction in v by a factor of approximately 4; the solute velocity in the mobile domain is 26.6 cm/hr, similar to that for the saturated case (Section D.3.3). This is consistent with the mechanism of rate-limited mass transfer that has been demonstrated in silt-textured sediments for unsaturated moisture conditions with mobile-immobile water (Gamerding et al. 2001a).

Figure D.3.4.3. Cs^+ Transport Through the "Above B" Composite Sediment at 23% Moisture Saturation and an Average Pore Water Velocity of 4.85 cm/hr.

Note: Compared with Figure D.3.4.2B, decreasing the velocity by a factor of approximately 4 resulted in increased sorption of Cs^+ . The observed retardation is **less** than predicted based on transport in saturated columns.

D.3.4.4 Conclusions and Implications

Cesium (Cs^+) transport was determined in unsaturated laboratory columns at 66% and approximately 24% moisture saturation. Re-packed sediment columns were equilibrated with a 5 M solution of NaNO_3 ; Cs^+ was applied as CsI at a concentration of 5.4×10^{-5} M (approximately 14 mg/L). The geochemical conditions were comparable to those used in other S&T Program investigations reported in Sections D.3.1 and D.3.3.

At 66% moisture saturation, Cs^+ retardation and transport were well predicted from Cs^+ retardation that was determined in saturated columns. At this higher water content (greater than 50% moisture saturation), the hydrodynamics are similar to a saturated system in that all of the water is associated with a single, mobile, flow domain. This is significant because it adds to the limited database indicating that transport at water contents greater than approximately 50 to 60% moisture saturation is predicted from transport behavior in saturated systems. This result

also provides further validation of the centrifuge method as an approach for studying transport through unsaturated sediments.

At approximately 24% moisture saturation, more than 80% of the pore water was associated with a stagnant, or immobile water domain. This hydrodynamic condition is characterized with a two-region (mobile-immobile) transport model and is consistent with other research indicating a significant fraction of immobile water at lower water contents (less than 30% moisture saturation). At 26% saturation and approximately the same velocity as for 100%, Section D.3.3, and 66% saturation, Cs^+ retardation and transport was poorly predicted from retardation that was determined in saturated columns; Cs^+ mobility was accelerated by a factor of 2. When velocity was reduced by a factor of 4, such that the velocity in the mobile domain approximated that for the saturated condition, retardation increased and was more consistent with predictions based on transport in saturated columns. For the hydrodynamic conditions obtained in the "Above B composite sediment, there was no evidence of disconnected pore water, consistent with other results for sediments with silt-sized particles. It was not possible to evaluate the effect of disconnected pore water (solutes completely excluded from a fraction of the pore space) on Cs^+ transport, which can result in transport that is accelerated by a factor of 2, regardless of the pore water velocity.

This research demonstrates that solutes that are transported via the mobile water domain in unsaturated sediments have limited access to sorption sites that are associated with the immobile water domain. Sorption is reduced and transport is further accelerated, (e.g., to a greater extent than restricting transport to the mobile water domain). This has important implications for our general understanding of sorption during transport in unsaturated sediments and interactions between hydrodynamic and geochemical processes. The results are consistent with a rate-limited mass transfer mechanism that is specific to unsaturated sediments where a significant fraction of water is associated with the immobile water domain. This is of particular importance to contaminant transport through the vadose zone at Hanford, and may be one of several factors that contribute to accelerated contaminant transport.

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D.3.5 MINERALOGIC RESIDENCE OF ^{137}Cs IN CONTAMINATED SEDIMENTS

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D.3.5.1 Introduction

The mineralogic residence of ^{137}Cs is a significant factor in determining its future mobility: micaceous minerals are much more energetic binders of Cs than other common silicates. The coarse-textured, micaceous sediments that make up the regional surface deposits underlying the SX tank farm (Tallman et al. 1979; Freeman-Pollard et al. 1994), have to large degree sorbed and concentrated the $^{137}\text{Cs}^+$ from leaked tank waste, limiting vertical migration to distances of approximately 6 – 20 m (20 – 65 ft). Because Cs^+ is soluble, the retardation of Cs^+ movement in vadose zone pore water and underlying groundwater is controlled by sorption, and Cs^+ is preferentially sorbed by phyllosilicate minerals, which include expandable layer silicates such as smectite and vermiculite, and non-expandable micas, such as biotite and muscovite.

The sorption of Cs to phyllosilicates has been actively researched since the advent of anthropogenic ^{137}Cs in the environment (Sawhney 1970; Evans et al. 1983; Comans and Hockley 1992; Corniell 1993). The consensus on the retention of $^{137}\text{Cs}^+$ by sediments is that frayed edge sites (weathered sites at the edges of mica flakes) strongly bind Cs^+ , preventing its rapid re-release. In the sub-tank sediments at Hanford, where micaceous minerals are common, it is not clear that sorption to micas has controlled ^{137}Cs mobility. Other reactions, such as Cs^+ incorporation into authigenic zeolites or aluminosilicates formed by waste-sediment interaction could also be significant. We investigated the retention of ^{137}Cs by individual particles within contaminated sediments from SX-108 slant borehole and 41-09-39 without preconception about which mineral phases would prove to be radioactive. After screening, individual radioactive particles were isolated and examined to determine their mineralogy. The initial work was conducted using samples from borehole 41-09-39 (McKinley et al. 2001), and subsequent work was done with samples from SX-108 slant borehole.

D.3.5.2 Experimental Procedures

Sediments from borehole 41-09-39 were examined that had been size fractionated by wet sieving. SX-108 borehole samples were not sieved. Sediments from both boreholes were disseminated onto glass slides and fixed, using collodion in amyl acetate. Individual radioactive particles were identified using either a Fujifilm BAS-5000 (25 μm resolution) or Molecular Dynamics Storm (50 μm resolution) digital autoradiography system. The phosphor-plate media were exposed to disseminated sediments to construct a "map" of radioactive particles for each sample slide. Particles identified as "positive" or "negative" with respect to radioactivity were then removed to separate slides, and the exposure was repeated to confirm whether the identifications were correct. Finally, single radioactive particles were separated and mounted individually. Individual particles were identified mineralogically using optical microscopy, and in some cases examined by scanning electron microscopy. For 41-09-39, individual micas were removed from the 106-250 μm and 250-500 μm size fractions, identified by color as biotite (black), vermiculite (rust), or muscovite (clear), and used to test the hypothesis that all micas

were radioactive because they preferentially retained ^{137}Cs . The individual mica particles were also counted for gamma activity in a low-level counting facility at the National Institute for Standards and Technology at Gaithersburg, Maryland.

D.3.5.3 Results

Inspection of the digitized phosphor-plate images provided a means of rapid detection and identification of $^{137}\text{Cs}^+$ -sorbing particles. Individual clasts were classified as “positive” (generating a radiological response) or “negative.” In 41-09-39, sediment clasts that showed positive autoradiography results were morphologically and mineralogically distinct from negative clasts. As shown in Figure D.3.5.1a, from the 53 - 106 μm fraction, but consistent with results from all the size fractions, the negative clasts were predominantly particles of **quartz** and plagioclase feldspar, with some surface staining by fine iron oxide. The positive clasts consisted of mineral fragments bound together by clay-sized materials, presumably smectite. The positive clasts were also consistently larger than the maximum size nominally allowed by the sieving procedure: they were relatively large agglomerates of finer clasts cemented by smectite (Figure D.3.5.1b). Smectite apparently flocculated during or after the wet sieving process, forming agglomerates with other phases and yielding anomalously large grain sizes. Close examination of the agglomerates showed an abundance of mica. The grains in Figure D.3.5.1b were partially disaggregated during manipulation, revealing the presence of micas as either translucent large flakes or as small, dark constituent flakes at the surface of the clumped material. Individual non-micaceous silicate grains were also separated from the clumps. These grains were of size comparable to negative grains in Figure D.3.5.1a. Examination of disaggregated positive grains using optical and electron microscopy showed them to consist of quartz and plagioclase, as well as mica and smectite. Some agglomerated samples were crushed and their components screened autoradiographically (data not shown); smectite separated from these particles did not give positive results.

The examination of positive clasts from 41-09-39 suggested that the selection of individual clasts for single-clast autoradiography and gamma counting might be biased toward agglomerated small particles, since the strongest radiological results would tend to come from relatively large clumps including numerous positive components. We determined the relative significance of different components by logically evaluating the autoradiography results and by performing additional autoradiography measurements. The primary silicates (quartz and feldspar) could be ruled out as sources of radiation by analogy to negative clasts. The retention of $^{137}\text{Cs}^+$ by micas was tested directly by picking mica flakes from the 0.106 - 0.250 mm and 0.250 - 0.500 mm size fractions (Figure D.3.5.2). The micas were all confirmed to significantly retain $^{137}\text{Cs}^+$ by producing visible radiation-induced spots on autoradiography plates. Biotite and vermiculite showed strongly positive results, with muscovite retaining less $^{137}\text{Cs}^+$ than the other micas. During physical manipulation, “vermiculite” flakes often delaminated, and were observed to consist of a rusty cover or sheath of vermiculite over a relatively pristine core of biotite. The retention of $^{137}\text{Cs}^+$ that was ascribed to vermiculite was resulted from retention by biotite or a composite of biotite and vermiculite. The three micas, in any case, showed a higher affinity than all other phases for $^{137}\text{Cs}^+$.

Figure D.3.5.1. Comparison of Positive (Radioactive) Sediment Grains with Negative (Non-Radioactive) Grains From Borehole 41-09-39, 53 – 106 μm size Fraction.

Note: Negative grains are monomineralic silicates; Positive grains are clay-cemented agglomerates containing mica flakes (arrows).

Figure D.3.5.2. Comparison of Autoradiography Results From Single Mica Flakes.

Note: Notations are: 106-250, etc. sieve-size sediment fractions from which micas were picked; Black: Biotite, Rust: Vermiculite, Trans: Muscovite. Each digital autoradiograph is paired with a Macroscopic Photomicrograph of the slide from which it was developed. Each slide contained six Mica flakes, circled. The density of the autoradiography spots is proportional to the activity of the imaged flakes.

Results for SX-108 slant borehole identified mica as the only significant retainer of ^{137}Cs (Figure D.3.5.3). All of the negative grains were non-micaceous silicates, as was the case for 41-09-39 samples. Since these sediments were not size-fractionated by wet sieving, no flocculation occurred. All of the positive grains were micas, with some micas including a small mass of adhering smectite.

The autoradiography method was used to identify radioactive particles, but could not discriminate between alpha, beta, and gamma radiation. The origin of detected radiation and its activity were confirmed by using low-level gamma counting. The integration of the single-grain exposure intensities (pixel densities) on autoradiography images provided a numerical value for radiation intensity (denoted photostimulated luminescence [PSL] **units**). These numerical results had good correspondence to gamma counting measurements of ^{137}Cs (Figure D.3.5.2; $r^2 = 0.83$). PSL intensities may have originated from beta or gamma radiation or both. The decay of ^{137}Cs to metastable ^{137}Ba includes emission of a 0.514 MeV β^- and a neutrino, followed by the isomeric transition of the ^{137}Ba by emission of a 662 KeV γ photon, detectable by gamma counting (Lederer et al. 1978). PSL measurements were more sensitive than gamma counting, and thus could estimate ^{137}Cs activities that were detectable by the phosphor system when these same activity levels were too small to be detected by gamma spectrometry (Figure D.3.5.4) (Zeissler et al. 2001).

Although all of the categorically positive clasts for SX-108 slant borehole were micaceous and all of the categorically negative clasts for both boreholes were silicates other *than* phyllosilicates, the clasts from the two boreholes were slightly different in their autoradiography results. The negative clasts from 41-09-39 were below detection (i.e., emitted less than approximately 0.05 Bq). Many of the negative clasts from SX-108 slant borehole, however, yielded **a** faint positive signal (Figure D.3.5.5). These clasts were examined by SEM to determine whether a secondary phase capable of retaining ^{137}Cs was present. Photomicrographs of **quartz** clasts from samples 03 (Figure D.3.5.6) and 07 (Figure D.3.5.7) show the presence on grain surfaces of numerous but very small (less than 10 μm) secondary crystals. These minerals have blocky habits and a composition (Na, Al, Si, O by energy dispersive spectroscopy, inset in Figures D.3.5.6 and D.3.5.7) that was consistent with zeolites identified in laboratory experiments of mineral-waste interaction performed with caustic tank-waste simulants (Section D.1.1). The retention of ^{137}Cs by the observed phases could not be confirmed; however, zeolites can sorb Cs^+ and the presence of ^{137}Cs on these clasts suggests that this phase may be responsible.

The absence of radioactivity on “negative” grains from 41-09-39 samples was puzzling. The samples examined from that borehole, however, had been size fractionated by sieving in the presence of water. It is possible that zeolites present on the surfaces of silicate clasts were either solubilized or physically removed during the sieving procedure. Alternatively, OH^- concentrations in the wastes that migrated through the 41-09-39 sediments may have been too low to induce significant mineral dissolution and precipitation.

Figure D.3.5.3. Photomicrographs of Particles Screened Using Digital Autoradiography to Identify Minerals Retaining ^{137}Cs .

Note: Grains that were identified as non-radioactive are denoted negative, and radioactive grains are positive. All negative grains are non-micaceous silicates, and all positive grains are micas alone or micas with minor adhering smectite.

Figure D.3.5.4. Comparison of Photostimulated Luminescence Data to Low Level Gamma Counting Results.

Note: The autoradiography method detected radioactive particles at a level below the detection limit low-level gamma counting which was ca. 0.01 Bq. Gamma counting confirmed that radiation was emitted by the decay of ^{137}Cs .

Figure D.3.5.5. Autoradiograph of Clasts From SX-108 that were Previously Screened and Mapped as “Positive” or “Negative.”

Note: The image brightness has been adjusted to show faint positive signals from negative grains.

Figure D.3.5.6. SEM Images of a Quartz Grain in SX-108 Sample 03, Showing the Presence on the Grain Surface of Secondary Minerals, Apparently Zeolite.

Figure D.3.5.7. Secondary Zeolite on the Surface of a Quartz Grain From SX-108 Sample 07.

D.3.5.4 Conclusions and Implications

This study confirms the preferential retention of ^{137}Cs by micaceous minerals in the SX tank farm sediments. ^{137}Cs was concentrated in micas during the interaction of tank wastes with sub-tank sediments, to the exclusion of more abundant smectites. The competitive retention of Cs by micas is consistent with the published observations of strong binding by micas in both the laboratory and contaminated settings. No other mineral phases were found to significantly sorb $^{137}\text{Cs}^+$ from tank waste. Small activity was associated with minute zeolite crystals on the surfaces of some silicates such as quartz. These zeolites may have precipitated during alkaline waste-sediment reaction and retained some $^{137}\text{Cs}^+$.

The future release of fluids to the SX tank farm vadose zone through waste retrieval or infiltration could pose a threat of $^{137}\text{Cs}^+$ remobilization. Our studies of the mineralogic residence of sorbed $^{137}\text{Cs}^+$ support the following implications. First, the competitive desorption of $^{137}\text{Cs}^+$ may be limited by the strong preference of micas for Cs^+ over other cations. Second, $^{137}\text{Cs}^+$ desorbed from micas and sparse zeolites may be rapidly resorbed by previously unimpacted sediments downgradient from the site of desorption; the presence of high-energy sites on these micas may effectively remove $^{137}\text{Cs}^+$ from dilute solutions.

D.3.5.5 Acknowledgement

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D.3.6 DESORPTION AND LEACHING OF CS+ FROM WMA S-SX SEDIMENTS

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D.3.6.1 Introduction

The Cs⁺ sorption process in geologic materials consists of a forward adsorption reaction and backward desorption reaction. Both of these reactions can be characterized by a two stage kinetic process: a fast reaction related to accessible external sites associated with the basal planes of 2:1 clay minerals (e.g., smectite, vermiculites, etc.) and a slow, diffusion controlled transport to/from frayed edge sites (FES) of micas (Zachara et al. 2001; Cornell 1993; Comans and Hockley 1992; Comans et al. 1991; Evans et al. 1983). Contrary to earlier conclusions, Cs does not seem to exchange with dehydrated interlayer sites of micas (Cornell 1993; Comans et al. 1991). Investigations by Coleman and Le Roux (1965; as reported by Cornell 1993) and Brouwers et al. (1983) have shown that Cs replacement is controlled by ion exchange equilibrium, and this equilibrium is reversible, albeit slowly, with time.

The vadose zone sediments in the S and SX tank farms are a complex mineral composite, including unstable primary phases (e.g., feldspars, micas, etc.) that are slowly weathering and more stable secondary phases (e.g., Al and Fe oxides, poorly crystalline SiO₂, and smectites). The harsh nature of tank leaked fluids (high base, high Na concentrations etc.) from the tanks in SX farm has driven dissolution and precipitation reactions that occurred concomitantly with Cs adsorption. Because of the disparate rates of Cs adsorption and mineral dissolution-precipitation, Cs may have become occluded from the surrounding environment by precipitation of secondary minerals on the surfaces and edges of Cs bearing sorbents. This "armoring" against Cs desorption would limit the pool of sorbed Cs available for future mobilization and transport.

Here we report on new studies of Cs desorption from ¹³⁷Cs-contaminated WMA S-SX sediments. These studies investigated Cs desorption in batch and small column reactors with different exchanging cations (Na⁺, K⁺ and Rb⁺). The potential for particle armoring as a control on Cs desorption was evaluated using acid ammonium oxalate [(NH₄)₂C₂O₄] as the extractant. Time-dependent desorption is described by coupling the multi-site exchange model (discussed in Section D.3.1) with a radial diffusion model approximated by a pseudo-1st-order rate. These results provide insights into the time dependence of Cs release from WMA S-SX sediments.

D.3.6.2 Experimental Procedures

The collection and analyses of sediments from the SX-108 borehole and 41-09-39 borehole are discussed elsewhere (Seme et al. 2001a, b). Materials used in these investigations were SX-108 sediments 3A, 7A, and 8A and 41-09-39 sediments 6AB, 7ABC, and 9ABC. Subsamples of the field moist material were air-dried to a constant weight and sieved to pass a 2 mm mesh. Gravels greater than 2 mm were removed from the air-dried material during the sieving process. The sieved material was thoroughly mixed to obtain a homogeneous sample. Total ¹³⁷Cs activity for these sediments is reported in Section D.3.1 (Table D.3.1.4). However, the Cs inventory of the

sediments also includes the Cs isotopes ^{133}Cs , ^{135}Cs . The total Cs determined by mass spectrometry (discussed in Section D.6.1) is 23.72, 13.66, 16.02, and 0.877 nmoles Cs/g sediment for 7A, 3A, 7ABC, and 9ABC, respectively.

D.3.6.2.1 Cesium Desorption Experiments. Batch-type desorption experiments were performed by suspending approximately 0.5 g sediment in 5 g solutions of 0.5 mol/L KNO_3 , 0.5 mol/L RbNO_3 , or 0.25 mol/L $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in Oak Ridge centrifuge tubes. Tubes were sealed and agitated at 25 C. At prescribed time intervals (0.02, 0.10, 0.21, 1, 4, 8, 16, 32, and 47 days; $[(\text{NH}_4)_2\text{C}_2\text{O}_4$ extraction was followed for 64 days instead of 47 days]) tubes were centrifuged (5000 rcf for 10 min), about 0.5 mL supernate was removed to tared gamma counting tubes, weighed, and aqueous ^{137}Cs activity determined by gamma-ray spectroscopy. After counting, the solutions were returned to the centrifuge tubes and the samples mixed vigorously for several minutes, and then returned to slow agitation. Sediments 3A, 7A, 7ABC, and 9ABC were studied in duplicate. After 47 days, enough solid KNO_3 or RbNO_3 was added to each tube to increase the total K or Rb aqueous concentrations to 2 mol/L and the aqueous phase was monitored as before for an additional 8 days.

A second set of suspensions of each of the four sediments was prepared with the ammonium oxalate electrolyte for destructive sampling to allow determination of the aqueous concentrations of elements of interest, e.g., Fe, Al, Ba, Ca, Cr, K, Mg, Na, and Si. Each suspension was composed of 0.5 g of sediment and 5 mL of electrolyte. Duplicate suspensions were centrifuged at 5000 rcf for 30 minutes at selected time intervals (2.5 hours, 10 hours, 2 days, 8 days, 33 days, and 64 days). The supernatant was carefully transferred to a plastic syringe fitted with a 0.2 μm filter. The first 1 mL of filtrate was discarded and the remaining collected in a plastic tube. The $^{137}\text{Cs}_{\text{aq}}$ activity was determined as previously described. The filtrate was analyzed for concentrations of the elements previously mentioned using ICP-AES.

D.3.6.2.2 Cesium Leaching from Columns. Approximately 2g of air-dry sediments (7A, 8A, 6AB, 7ABC) were packed into 3.1 cm length by 0.78 cm diameter polypropylene columns. The columns were connected to a peristaltic pump on one side and a fraction collector on the other. They were continually leached with 0.5 mol/L NaNO_3 solution for about 25 to 30 pore volumes at a flow rate of 0.1 mL min^{-1} (residence time $\approx$ 6 min). Right before columns were connected to the leaching solution, 10 mL of pure CO_2 gas was injected through columns to displace the air from the sediment pore space. A uniform movement of the leaching solution through the packed, air-dried sediments was observed. Sediment leachates were collected every six minutes and the mass of collected solutions determined to better estimate flow rate. After all the leachates were collected, columns were flushed with 1.0 mol/L NaNO_3 or KNO_3 and the electrical conductivity monitored to estimate conservative tracer breakthrough. This procedure was followed by flushing the columns with deionized water, then weighing the columns, and determining the pore space as the difference between wet and air-dry sediments. The leachates were analyzed for ^{137}Cs via gamma-ray spectroscopy. Two additional columns, packed with sediments 7A and 7ABC, were leached as above but with 0.5 mol/L KNO_3 for 20 pore volumes followed by 0.25 mol/L $(\text{NH}_4)_2\text{C}_2\text{O}_4$ (adjusted to pH 3) for an additional 20 to 25 pore volumes; all other procedures were performed as described.

The effect of temperature on Cs leaching was studied using two columns (as described above) packed with SX-108 7A sediment. With the initial temperature set at about 15°C, 0.5 mol/L

NaNO₃ solution was passed through a column at 0.1 ml min⁻¹. Once a steady-state Cs effluent concentration was approximated (–100 min), a stop-flow event was initiated. After 2.5 h, flow was restored and effluent monitored to determine effluent return to a quasi-steady-state condition. At this point, the temperature was increased to about 35 °C, effluent monitored to determine return to a quasi-steady-state condition, where a stop-flow event was again initiated. This cycle was repeated once again at 55 °C. The second column followed a similar procedure except after initial leaching (–100 min) at 15 °C the temperature was increased to 55 °C. After a quasi-steady-state Cs concentration was obtained, a series of three stop-flow events were performed as before, but with the temperature being decreased (55 °C to 35 °C to 15 °C) after each event. Temperature changes were accomplished by submerging the column and the inflow line (about 2 m long) in a temperature-controlled bath, temperature equilibration was determined by monitoring the effluent temperature (–50 min).

D.3.6.3 Results

D.3.6.3.1 Cesium Desorption with 0.5 M KNO₃ or RbNO₃. The desorption of Cs resulting from exposure to 0.5 mol/L K- or RbNO₃ exhibited a rapid exchange between the surface Cs and K or Rb, followed by a continuous slow release of Cs from the surface (Figure D.3.6.1). Generally, RbNO₃ solutions caused greater exchange of Cs between the sediment and the solution during the initial 24 hours. This results from the higher selectivity of Rb over K and is related foremost to the hydration energies of the cations, K greater than Rb greater than Cs (Cornell 1993). The exception to this trend is observed for tank SX-108 sample 3A. This sediment is one of the most highly weathered sediments collected; scanning electron microscopy (Section D. 1.1) shows deteriorated mica edges, surface pits, and copious secondary mineral phases. Mineral alteration may have changed the relative exchange affinities of Cs, K, and Rb.

Further Cs release, after the initial 47-day equilibration, was affected by increasing the [K]_{aq} or [Rb]_{aq} concentrations to 2 mol/L (Figure D.3.6.1). After electrolyte addition, the sediments exhibited the same type of desorption profile observed after the first electrolyte addition; that is, a rapid exchange followed by continuous slow release. However, sediments 3A and 7A displayed unusual behavior. The addition of 2.0 mol/L KNO₃ released more Cs from the 3A sediment than Rb, even though at 47 days the two cations had exchanged the same quantity of Cs. For 7A, the 2.0 mol/L K- and RbNO₃ desorbed the same amount of Cs after 8 days, but Rb was far more competitive for Cs than K was at the initial 0.5 mol/L concentration. Both of these findings were unexpected, and, at this point, the cause(s) remain unresolved.

Figure D.3.6.1. Desorption of $^{137}\text{Cs}^+$ From WMA S-SX Sediments as a Function of Exchangeable Cation (K or Rb), Time and Ionic Strength (less than 47 days, K^+ or $\text{RbNO}_3 = 0.5 \text{ mol/L}$; greater than 47 days, K^+ or $\text{RbNO}_3 = 2.0 \text{ mol/L}$).

The percentage of Cs that was desorbed over the first two days (arbitrarily set as the initial exchange) varied with exchange cation (K or Rb) and sediment (Table D.3.6.1). With the exception of sediment 3A, the RbNO₃ solution extracted more Cs than KNO₃. The interesting point about these data was the apparent incongruity regarding Cs release from 9ABC. This sediment had the lowest mole fraction Cs (X_{Cs}) on the exchange complex of any of the sediments investigated; $\log X_{Cs} = -3.75, -3.82, -3.81$ and -4.95 for 7A, 3A, 7ABC, and 9ABC, respectively. This X_{Cs} translates into almost a 0.5 log unit increase in Cs⁺ binding affinity for 9ABC as measured by a conditional exchange constant, K_c (Section D.3.1). Increased binding affinity should translate to a smaller percentage of Cs desorbed from this sediment. In addition, the adsorption density (X_{Cs}) in the other three sediments were relatively similar, and therefore should release comparable concentrations of Cs. Yet, the ~~tar~~ SX-108 sediments lagged behind the other sediments in the percentage Cs released.

Table D.3.6.1. Percentage of ¹³⁷Cs Desorbed During the Initial Exchange with 0.5 mol/L K- or RbNO₃ and 2 mol/L K- or RbNO₃.

Sediment	0.5 mol L ⁻¹		2 mol L ⁻¹	
	K	Rb	K	Rb
	%			
sx-108				
7A	14.1	16.7	18.2	20.0
3A	17.0	16.6	21.5	20.1
41-09-39				
7ABC	17.7	22.4	24.1	25.5
9ABC	17.5	24.1	20.6	28.7

The interaction of (NH₄)₂C₂O₄ with the same four sediments extracted 44.6%, 60.8%, 55.9%, and 44.1% of the Cs after 64 days for 7ABC, 9ABC, 3A, and 7A, respectively (Figure D.3.6.2; Table D.3.6.2). All of the sediments exhibited signs of continued release of Cs to at least 64 days unlike the results within K- or RbNO₃. The use of (NH₄)₂C₂O₄ was based on two premises: (1) layer lattice silicates exhibit similar selectivities for the NH₄⁺ and K⁺ ions (Bruggenwart and Kamphorst 1979) and (2) (NH₄)₂C₂O₄ dissolves poorly crystalline oxides without significant damage to layer silicates if limited to about 2-hours (Loeppert and Inskeep 1996). From the percentage of total solids dissolved after 33 days (Table D.6.3.2), the extraction cannot be considered benign. However, the initial [Cs]aq activity that was determined at 2.4 hours (Table D.3.6.2) showed substantially greater Cs release than KNO₃ (approximately 7%) or RbNO₃ (approximately 4%). Because ion selectivity increases as Cs⁺ > Rb⁺ > K⁺ ≈ NH₄⁺, the larger initial [Cs]aq concentrations observed in the (NH₄)₂C₂O₄ solutions suggested that secondary mineral precipitates were dissolved that allowed greater exchange of the sorbed ¹³⁷Cs. The action of the (NH₄)₂C₂O₄ in dissolving poorly crystalline oxides appears to expose Cs

containing surface and edge sites to exchange with the NH_4^+ cation. While Cs containing mineral particles coated with secondary mineral precipitates resulting from waste-sediment reactions and natural weathering inhibits Cs^+ exchange with the aqueous phase, the amount of Cs armored against exchange appears to be minimal.

Table D.3.6.2. Percentage of ^{137}Cs Released to Solution by $(\text{NH}_4)_2\text{C}_2\text{O}_4$, KNO_3 and RbNO_3 at Selected Times and the Percentage of Solids Dissolved After 33 Days Exposure to 0.25 mol/L $(\text{NH}_4)_2\text{C}_2\text{O}_4$.

Sediment	^{137}Cs Released					Solids Dissolved'
	$(\text{NH}_4)_2\text{C}_2\text{O}_4$			KNO_3	RbNO_3	$(\text{NH}_4)_2\text{C}_2\text{O}_4$
	2.4 hr	33 days	64 days	2.4 hr	2.4 hr	33 days
41-09-39						
IABC	21.3	40.0	44.6	13.8	17.3	2.03
9ABC	19.6	52.5	60.8	12.3	16.2	1.73
SX-108						
3A	19.5	49.2	55.9	12.8	13.6	2.41
7A	19.3	37.4	44.1	12.1	15.2	2.11

D.3.6.3.2 Kinetic Modeling of Cs Desorption in K and Rb Electrolytes. The kinetic data for Cs desorption by 0.5 mol/L KNO_3 or RbNO_3 (Figure D.3.6.1) was simulated based on the assumption that Cs in the contaminated sediments consists of three populations: equilibrium-controlled exchangeable Cs, kinetic-controlled exchangeable Cs, and a Cs pool termed "non-exchangeable" (this pool includes Cs armored against exchange discussed above). Similar models have been used successfully to simulate ^{137}Cs transport in undisturbed soil columns contaminated during the Chernobyl accident (Toso and Velasco 2001). Assuming that the kinetic-controlled exchangeable Cs can be modeled using a first order rate law, then Cs desorption can be described as

$$[\text{Cs}]_{\text{aq}} = [\text{Cs}]_{\text{aq}}^{\text{eq}} - [\text{Cs}]_{\text{aq}}^{\text{kinetic}} \quad (\text{D.3.6.1})$$

$$\frac{d[\text{Cs}]_{\text{aq}}^{\text{kinetic}}}{dt} = k_1 ([\text{Cs}]_{\text{aq}}^{\text{kinetic}}(t=0) - [\text{Cs}]_{\text{aq}}^{\text{kinetic}}) \quad (\text{D.3.6.2})$$

where $[\text{Cs}]_{\text{aq}}^{\text{eq}}$ is the equilibrium-controlled exchangeable Cs, $[\text{Cs}]_{\text{aq}}^{\text{kinetic}}$ is the kinetic-controlled exchangeable Cs, $[\text{Cs}]_{\text{aq}}^{\text{kinetic}}(t=0)$ is the maximum kinetic-controlled exchangeable Cs, and k_1 is the first order rate constant. Equations D.3.6.1 and D.3.6.2 can be solved to obtain

Figure D.3.6.2.

$$[Cs]_{aq} = [Cs]_{aq}^{exch} - [Cs]_{aq}^{kinetic}(t=0)\exp(-k_1 t) \quad (D.3.6.3)$$

where $[Cs]_{aq}^{exch}$ is the total amount of exchangeable Cs (including equilibrium- and kinetic-controlled exchangeable Cs). Model (3) contains three parameters: the total amount of equilibrium- and kinetic- controlled Cs, and the rate parameter k_1 . These 3 parameters were estimated by fitting to experimental data. Because the $[Cs]_{aq}^{exch}$, and $[Cs]_{aq}^{kinetic}$ were estimated from data with specific ionic strength and sample conditions, an ion exchange model (Section D.3.1) was used in back-calculating the total exchangeable Cs and total kinetic-controlled exchangeable Cs.

D.3.6.3.3 Cs Ion Exchange Model. The Cs ion exchange simulation was based on a 2-site model with its parameters determined previously or from the literature (exchange parameters between Cs, Na, and K were extracted from Zachara et al. [2001]; exchange parameters between Rb and Cs or Na or K were taken from Brouwers et al. [1983]). For each value of $[Cs]_{aq}^{exch}$ or $[Cs]_{aq}^{kinetic}$ estimated from the kinetic model, a corresponding total exchangeable or kinetic-controlled Cs concentration, $[Cs]_{aq}^{exch}$ or $[Cs]_{aq}^{kinetic}$, was calculated from the exchange model as described below.

Cs-Mi exchange on site I (Mi = Na, K, Rb)

$$N_{Mi}^I [Cs^+] K_c^I (Cs - Mi) = N_{Cs}^I [Mi^+] \quad (D.3.6.4)$$

Cs-Mi exchange on site II

$$N_{Mi}^{II} [Cs^+] K_c^{II} (Cs - Mi) = N_{Cs}^{II} [Mi^+] \quad (D.3.6.5)$$

Mass balance on exchange site I

$$N_{Cs}^I + \sum_{i=1}^L N_{Mi}^I = 1 \quad (D.3.6.6)$$

Mass balance on exchange site II

$$N_{Cs}^{II} + \sum_{i=1}^L N_{Mi}^{II} = 1 \quad (D.3.6.7)$$

Mass balance of Cs

$$(E_I N_{Cs}^I + E_{II} N_{Cs}^{II}) CEC W_s + V [Cs^+] = T_{Cs} W_s \quad (D.3.6.8)$$

Mass balance of Mi

$$(E_I N_{Mi}^I + E_{II} N_{Mi}^{II}) CEC W_s + V[Mi^+] = T_{Mi} W_s \quad (D.3.6.9)$$

where N_{Cs}^I and N_{Mi}^I are the equivalent fractions of Cs and Mi on site I, respectively; N_{Cs}^{II} and N_{Mi}^{II} are the equivalent fractions of Cs and Mi on site II, respectively; E' and E'' are the equivalent fractions of site I and site II with regard to the total soil CEC; W_s is the dry soil weight, V is aqueous volume, and T_{Mi} is the total initial concentrations of Mi in soil; K_c^I and K_c^{II} are conditional exchange constants on site I and site II, respectively; N_i^I and N_i^{II} are the equivalent fraction of ion Mi on site I and II, respectively; $[Mi]$ is the aqueous concentration of Mi in solution; and (Cs^+) is the aqueous concentration of Cs, which equals $[Cs]_{aq}^{exch} W_s/V$ or $[Cs]_{aq}^{kinetic} W_s/V$. The calculated TCs was the total Cs concentration corresponding to $[Cs]_{aq}^{exch}$ or $[Cs]_{aq}^{kinetic}$.

The above kinetic model well described experimental results out to about 16 days (386 hours, Figure D.3.6.3) with estimated parameters summarized in Table D.3.6.3. For all sediments, several general trends were pertinent to the above analysis.

Table D.3.6.3. Estimated Properties for the Three-Site (pool) Cs Desorption Model.

	K		Rb		K	Rb
	Exchangeable	Kinetic Fraction	Exchangeable	Kinetic Fraction	Overall mass	Overall mass
	¹³⁷ Cs(pCi/g)				transfer rate (per hour)	
SX-108 07A	3.05×10 ⁷	2.42×10 ⁶	1.17×10 ⁷	1.70×10 ⁶	0.009	0.009
SX-108 03A	1.79×10 ⁷	6.14×10 ⁶	6.38×10 ⁶	1.50×10 ⁶	0.026	0.019
41-09-39 7ABC	2.22×10 ⁷	5.81×10 ⁶	1.03×10 ⁷	2.96×10 ⁶	0.02	0.019
141-09-399ABC	1.26×10 ⁶	4.39×10 ⁵	5.91×10 ⁵	2.56×10 ⁵	0.029	0.026

First, the total K-exchangeable Cs was required to be between 19 to 23% of the total Cs on the exchange complex in order to achieve reasonable model simulations, while the total Rb-exchangeable Cs was required to be between 19 to 27% of the total Cs. This small difference in the computed exchangeability of Cs in the K^+ and Rb^+ electrolyte reflect the difference in selectivity of Rb, K, and Cs and that the Rb exchange coefficients were not determined for the geologic materials, but rather, extracted from the literature. In addition, the calculated percentages of K and Rb exchangeable Cs could be affected by: (1) potential CEC errors used in the model (Na-CEC was used and actual samples may contain higher CECs because K, Rb, and Cs can occupied more sites than Na); and (2) other cations present in solution that were not considered in the ion exchange calculation, but may affect Cs displacement, such as Ca^{2+} .

Figure D.3.6.3. Aqueous Exchange Data and Results of Three-Site Model Simulations for KNO_3 or RbNO_3 Exchange with ^{137}Cs Contaminated Sediments a) SX-108 3A, b) SX-108 7A, c) 41-09-39 7ABC, and d) 41-09-39 9ABC.

Second, the overall mass exchange coefficient (pseudo-1st order rate coefficient) for the kinetic-controlled exchangeable Cs indicated a slow Cs desorption step (rate constant ranges between 0.01-0.03 h⁻¹, or a $t_{1/2}$ = 23.1 and 69.3 hours). This slow Cs desorption is attributed to a film diffusion of Cs from a sorbed site to the bulk aqueous phase. Reported literature values of Cs adsorption and desorption rate coefficients range widely depending on the models and experimental procedures used. Generally, the kinetics of ion exchange can be divided into three individual processes (Sposito 1994): (1) film diffusion, which is ion diffusion from bulk solution to sorption sites; (2) kinetic complexation reactions at sorption sites; and (3) ion diffusion into intraparticle sorption sites. The desorption process is simply the reverse. Based on an experimental procedure developed by Ogwada and Sparks (1986), Liu et al. (1994) modeled rate coefficients for these individual processes for illite-containing and montmorillonite-containing soils. The determined rate coefficients were film diffusion 0.24-0.96/hr (half-life = 0.72⁻³ hours), intraparticle diffusion 1.68-3.84/hr (half-life = 0.18-0.42 hours), and kinetic sorption 10.8 hr (half-life = 0.06 hours). Based on the determined rate coefficient for film diffusion, Liu et al. (1994) calculated that the film diffusion coefficient was between 4.8-5.2 × 10⁻¹² cm²/s. The rate coefficient for the present study, based on our modeling results, was approximated by a film diffusion process, suggesting that film diffusion may be the rate-limiting process for Cs release from the Hanford sediments.

Coman and Hockley (1992) studied the long-term kinetic behavior of Cs and found that the kinetic sorption of Cs on illite could be divided into two steps. The fast sorptioddesorption of Cs was suggested to be between bulk solution and surface sorption sites with a rate constant about 0.04-0.4/hr (half-life = 1.7-17 hours). This was followed by a slow step of Cs “fixation” with a rate constant of about 0.00015-0.0002/hr (half-life = 3465-4620 hour). The rate coefficient of the fast sorptioddesorption step was close to our value (0.01-0.04/hr). However, Cs desorption in the current study appears to continue for greater than 30 days. In the current studies, the initial exchange and fast desorption step (modeled data), was followed by a long-term, slow desorption period similar to that observed by Coman and Hockley (1992) suggesting that the Cs “fixation” was reversible, but with a smaller rate than previously reported.

The later desorption data (8 to 47 days) for the all sediments was used to estimate a first-order rate constant (Table D.3.6.4) for the slow desorption process. The calculated rate constants define an extremely slow process, and one that is far reduced below that expected by film diffusion. The $t_{1/2}$ calculated from the pseudo-1st order rate constants illustrate the slowness of this reaction (Table D.3.6.4). Our results are less than an order of magnitude smaller than that observed for illite (Coman and Hockley 1992). The slowness of this observed desorption process is thought to result from the long inground exposure (greater than 30 years), the elevated temperature of the sediments during aging (50 to 80 °C), and the harsh chemical environment caused by the leaked fluids (hyperalkaline, hypersaline). It is significant that the $t_{1/2}$ for 9ABC was substantially less than that of the other sediments. Based on the concentrations of the other contaminants (e.g., Cr, Tc, Na), 9ABC appears to have been far less affected by the leaked tank wastes.

Table D.3.6.4. Pseudo-First Order Rate Constants and Half-Lives of the Slow Desorption Reaction Observed in WMA S-SX Sediments.

Sediment	Exchange Cation	Rate Constant per day	$t_{1/2}$ days
SX-108			
7A	K	4.14×10^{-4}	1674
	Rb	5.55×10^{-4}	1247
3A	K	5.63×10^{-4}	1232
	Rb	5.69×10^{-4}	1218
41-09-39			
IABC	K	5.51×10^{-4}	1258
	Rb	9.75×10^{-4}	710
9ABC	K	6.94×10^{-4}	998
	Rb	1.39×10^{-4}	500

Our kinetic model was developed by utilizing aqueous ^{137}Cs data generated from the 0.5 moVL K- or RbNO_3 exchange studies (Figure D.3.6.1). The data allowed the calculation of the total sediment Cs concentrations for the different sorbed populations considered by the model (Table D.3.6.3). The model and its fitted population estimates were used to simulate the desorption of ^{137}Cs from the same four sediments in the presence of increased electrolyte added after 47 days (2.0 mol/L K- or RbNO_3 Figure D.3.6.4; K data only). The Cs $\rightarrow$ K exchange-desorption was well described by the model in all four sediments without any parameter adjustment. The model clearly embodies the primary features and phenomenology involved in the desorption process. From these results, we estimate that: (1) the exchangeable pool represents 20 to 30% of the total sediment Cs, (2) the kinetic fraction represents 20 to 35% of the total sediment Cs, and (3) the long-term fraction (by difference) represents 35 to 50% of the total sediment Cs. Of this latter fraction, it appears that only 6% to 10% can be directly attributable to secondary mineral precipitation related occlusion.

Figure D.3.6.4. Aqueous Exchange Data and Results of Three-Site Model Simulations for KNO_3 or RbNO_3 Exchange at 0.1 M (0 to 47 days) and 2.0 M (47 to 64 days) with ^{137}Cs Contaminated Sediments.

D.3.6.3.4 Cs Leaching from Columns. The leaching profile of ^{137}Cs by 0.5 mol/L NaNO_3 as a function of pore volume (pv) was characterized by an initial flush of ^{137}Cs followed by a long tail of decreasing ^{137}Cs activities (Figure D.3.6.5). The initial pulse of ^{137}Cs activity from these columns was the result of Na^+ exchange for Cs^+ on the easily accessible exchange sites. However, residual Na associated with the leaked fluids may have increased Cs^+ exchange over that expected from 0.5 mol/L NaNO_3 . The residual Na concentration in these two sediments increased the initial Na_{aq} concentrations to at least 3.6 mol/L and 0.84 mol/L for 7A and 7ABC, respectively. While these quickly decreased (in 4-5 pv) to the influent Na concentration (0.5 mol/L), the initially high Na concentrations increased the initial flush of Cs over that expected for the influent solution. Sediment with 0.5 mol/L NaNO_3 or 5.0 mol/L NaNO_3 in batch mode showed that the higher electrolyte concentration solubilized ten-times more ^{137}Cs (see Section D.3.1, Figure D.3.1.4).

Despite the high initial flushing of ^{137}Cs , the total amount of Cs leached from the sediments was small compared to the total (Table D.3.6.5). For all columns, the initial four pore volumes accounted for about 1/3 of the Cs leached for the entire study and >1% of the total Cs. Four pore volumes represents that necessary to leach the residual Na from the columns. Based on modeling of the static-studies above (Figures D.3.6.3 and D.3.6.4), the Cs being leached from the columns was probably that associated with the easily exchangeable fraction, since the calculated diffusion-limited desorption rate constants for these sediments were small (0.01-0.03/hr, or a $t_{1/2}$ = 23.1- 69.3 hours). The residence time in these small columns was approximately 6 minutes; the entire study, up to the stopped flow event (at the 19" or 20" pore volume) took two hours. While stopping the flow for 19 hours did increase in Cs leaching, the increase in aqueous phase ^{137}Cs was small and transient. Depending on the mass transfer rates (film diffusion) for the individual sediments, the impact of 19 hours stopped-flow event is about what would be expected.

Table D.3.6.5. ^{137}Cs Activities (pCi/g) in 4 WMA S-SX Sediments, and Aqueous Concentrations (pCi/L and %) of ^{137}Cs Leached From Sediments by 0.5 mol/L NaNO_3 .

Sediment	Total ^{137}Cs sediment	^{137}Cs leached from sediments		^{137}Cs leached	
		Total	Initial ^a	Total	Initial'
		pCi/g		%	
7A	5.9×10^7	1.4×10^6	4.7×10^5	2.3	0.8
8A	5.6×10^5	4.7×10^3	1.4×10^3	0.8	0.3
6AB	8.3×10^4	9.6×10^2	3.5×10^2	1.2	0.4
7ABC	4.0×10^7	6.0×10^5	1.6×10^5	1.5	0.4

^aFirst 4 pore volumes

Figure D.3.6.5. ^{137}Cs Leaching Profile From Sediments, a) 41-09-39 7ABC, and b) SX-108 7A with 0.5 mol/L NaNO_3 .

The leaching of ^{137}Cs from sediments 7A and 7ABC by $0.5 \text{ mol L}^{-1} \text{KNO}_3$ was similar to the NaNO_3 system (Figure D.3.6.6). As with the static exchange studies (Section D.3.1, Figure D.3.1.4), K^+ displaced more $^{137}\text{Cs}^+$ than Na^+ . In comparison to Na^+ , K^+ leached almost ten times more $^{137}\text{Cs}^+$ in the initial 4 pore volumes and throughout the flow study (Table D.3.6.6). Given that the overall mass transfer rates for Na^+ , K^+ , and Rb^+ (see modeling results for K^+ and Rb^+ ; Table D.3.6.3) were similar and that the leaching observed in the columns was the result of ion exchange with easily accessible exchange sites, the difference between the NaNO_3 and KNO_3 columns may be attributed exclusively to the differences in K^+ and Na^+ exchange selectivity.

Figure D.3.6.6. ^{137}Cs Leaching Profile From Sediment SX-108 7A by a) 0.5 mol/L KNO_3 (initial; 20 pv), and b) $0.25 \text{ mol/L (NH}_4)_2\text{C}_2\text{O}_4$ (greater than 20 pv).

Sediment	¹³⁷ Cs in sediment	¹³⁷ Cs leached from column experiments				¹³⁷ Cs leached ^b			
		Total	Initial'	¹³⁷ Cs ^c	¹³⁷ Cs ^d	Total	Initial ^a	¹³⁷ Cs ^c	¹³⁷ Cs ^d
			pCi/g			%			
SX108									
7A	5.9×10 ⁷	5.9×10 ⁷	4.2×10 ⁶	1.1×10 ⁷	3.7×10 ⁶	25.1	7.1	18.8	6.3
7ABC	4.0×10 ⁷	8.3×10 ⁶	1.2×10 ⁶	4.2×10 ⁶	4.1×10 ⁶	20.8	2.9	10.5	10.3

The change of leaching solution from 0.5 mol/L KNO₃ to **0.25** mol/L (NH₄)₂C₂O₄ was designed to estimate the impact of secondary mineral overgrowth on Cs desorption (Figure **D.3.6.6**). As the (NH₄)₂C₂O₄ moved through the column, there was a smooth increase in Cs leaching followed by a return to almost the exact same leaching profile observed prior to its injection. While this may be fortuitous, more likely, it is a reflection of similar exchange selectivity coefficients between K⁺ and NH₄⁺. In these studies, unlike the long-term (100 day) (NH₄)₂C₂O₄ batch system, dissolution of minerals resulting from the low pH (pH 3) should not be of consequence (Loeppert and Inskeep **1996**) since the column residence time was short. Hence, these data suggest that the increased leaching of Cs was due to the removal of poorly crystalline oxides that blocked a fraction of Cs-containing sorption sites. The increase in Cs exchange related to oxide removal was about **6.3** and 10.3% of the total exchangeable Cs for sediments **7A** and **7ABC**, respectively, which is about that estimated from the batch studies discussed above.

The effect of increasing temperature on Cs release from columns packed with sediment **SX-108 7A**, after the initial flush of Cs (about 8 pore volumes), is shown in Figure **D.3.6.7**. As temperature was increased from 14 °C to 34 °C to 55 °C, steady-state Cs effluent concentrations quickly stabilized at increasingly greater concentrations. Conversely, as temperature was decreased in 10 °C increments, steady-state Cs effluent concentrations quickly stabilized at decreasing levels. While difficult to see from the plots in **D.3.6.7**, the maximal Cs concentration resulting from a 2.5 h stop-flow followed the same behavior as Cs steady-state concentrations with temperature change. The observed changes in effluent Cs concentration were smooth, and indifferent to the order of temperature change, suggesting that the governing reactions were unaffected by the small surface Cs concentration changes observed over the life of these studies.

Figure D.3.6.7. Column Cs Leaching and Stop-Flow Profiles for Sediment SX-108 7A by 0.5 mol/L NaNO₃ at Three Temperatures.

Two methods were used to calculate pseudo-first order rate coefficients from the column Cs data. One method assumed that a steady state concentration (and leaching rate) was obtained at each temperature during advective flow. A first-order model was fit using the leaching concentration and the column residence time. The second method used to calculate rate coefficients considered the concentration reached in solution during the stop flow event (2.5 hours). This static method uses the maximum concentration achieved during stop flow (as measured once flow was reinitiated). Rate constants and half-lives ($t_{1/2}$) for both methods are tabulated in Table D.3.6.7. The steady-state pseudo-first order rate coefficients are about an order of magnitude greater than those determined from stop-flow data. These differences are believed to arise due to advection continually removing mass from the column, causing greater diffusional gradients, and faster rates than typically observed for static (stop-flow) methods. Yet, it is the steady-state flow method that yields rate coefficients similar to those determined for the batch studies and modeling (Section D.3.6.3.3) for the kinetic-controlled exchangeable Cs (0.01 to 0.03 h^{-1} , or $t_{1/2} = 23.1$ to 69.3 h).

Table D3.67. Pseudo-First Order Rate Constants and half-life ($t_{1/2}$) as a **Function** of Temperature From Column Leaching of Cs For Sediment SX-108 7A.

Temperature (°C)	Rate Constant : Steady-State (h^{-1})	Rate Constant : Stop-Flow (h^{-1})	Steady-State $t_{1/2}$ (h)	Stop-Flow $t_{1/2}$ (h)
14	1.50×10^{-2}	1.07×10^{-3}	46.1	647
34	3.16×10^{-2}	1.85×10^{-3}	21.9	375
55	6.55×10^{-2}	3.70×10^{-3}	10.6	187
55	6.83×10^{-2}	4.29×10^{-3}	10.1	162
35	2.77×10^{-2}	1.76×10^{-3}	25.1	394
15	1.07×10^{-2}	6.85×10^{-4}	64.6	1011

Plotting the rate coefficients for steady-state and stop-flow data versus the reciprocal of temperature (in $^{\circ}\text{K}$) yields two Arrhenius plot whose slopes represents a measure of the effective activation energy ($E_{act,eff}$) for Cs release (Figure D3.6.8). The $E_{act,eff}$ for steady-state data were 15.5 kJ/mol and 19.5 kJ/mol for increasing and decreasing T, respectively; for stop-flow data $E_{act,eff}$ = 12.5 kJ/mol and 19.4 kJ/mol for increasing and decreasing T, respectively. The Arrhenius plots for these data show that (1) the direction of temperature change (increasing or decreasing) did not impact the slope, and (2) even though the two methods of determining rate coefficients yielded coefficients about an order of magnitude different, the Arrhenius plot slopes are essentially identical. The average $E_{act,eff}$ = 16.7 kJ/mol, which is only slightly greater than that typically reported for diffusion-controlled reactions (10 – 12 kJ/mol).

Figure D3.6.8. Arrhenius Plot (**log k vs. 1/T**) for Column Cs Leaching From Sediment SX-108 7A by **0.5 mol/L NaNO₃** at Three Temperatures Based on a) Stop-Flow Data (**▼,▲**) and b) Steady-State Flow Data (**V, A**).

Taken as a whole, the flow studies corroborate the results and conclusions of the previously discussed batch studies. The initial release of Cs appears to be governed by surface exchange sites and is a rapid reaction. The slower kinetic-controlled Cs exchange is diffusion controlled and appears very uniform with an $E_{act,eff}$ that is approximately that associated with diffusion-controlled reactions. In addition, the amount of Cs that is apparently armored by secondary precipitates against desorption is small; perhaps as much as 10%. While the Cs in the sediments is desorbable, the process is extremely slow.

D.3.6.4 Conclusions and Implications

- (1) Cs desorption may be simulated using a model containing three sorbed populations of Cs: (1) equilibrium-controlled exchangeable Cs, (2) kinetic-controlled (diffusion) exchangeable Cs, and (3) slowly exchangeable Cs. All three populations appeared to be exchangeable, although release from the latter pool was extremely slow ($t_{1/2} \approx 1000$ days).
- (2) While the cations Rb^+ , K^+ , and Na^+ exhibited different exchange selectivity coefficients (Rb greater than K greater than Na) against Cs, the concentrations of the kinetically controlled Cs populations were largely unaffected by cation type.
- (3) Based on modeling of batch desorption experiments, the easily exchangeable Cs pool was about 20 to 30% of the total Cs, the diffusion controlled Cs (or kinetic fraction) pool was approximately 20 to 35% of the total Cs, and the slowly exchangeable pool was 35 to 50% of the total Cs. Only about 10% of the slowly exchangeable Cs pool could be attributed to Cs occlusion by secondary mineral formation.
- (4) While the Hanford sediments have a high sorption affinity for Cs, approximately 50% of the sorbed ^{137}Cs is exchangeable with the aqueous phase and could be remobilized using solutions of highly selective cations (K or Rb) or high ionic strength.

The studies reported here were designed, for the most part, to maximize Cs desorption from contaminated sediments. Clearly, a pure K^+ or Rb^+ solution will not develop in the pore waters underlying the S and SX tank farms. However, the small column studies using 0.5 mol/L $NaNO_3$ may, in fact, reasonably mimic leaching conditions that may develop from accidental spills during tank waste removal or from meteoric recharge. Residual Na from leaked waste solutions are seen in most sediments studied. This residual Na will be mobilized during sediments upon rewetting, and as with the column studies, increase the $[Na]_{aq}$ concentrations above those normally observed in pore waters.

Even with elevated Na concentrations, only a small percentage of the sorbed ^{137}Cs inventory was leachable. After the initial flush of easily exchangeable ^{137}Cs , the desorbed concentrations of ^{137}Cs would rapidly decrease to concentrations controlled by film diffusion. The more recalcitrant Cs pool, will not contribute to Cs transport because of its extremely slow desorption kinetics. Dissolution of secondary minerals and the subsequent increase in easily exchangeable Cs, as seen with $(NH_4)_2C_2O_4$, should not occur in these sediments since the existing sediment pH is slightly basic and the secondary minerals are stable under the observed conditions. Even though the entire Cs pool is believed to be exchangeable with time, and therefore available for

transport, the **high** Cs exchange selectivity coefficients exhibited by underlying uncontaminated sediments will retard Cs transport.

D.3.6.5 References

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D.3.7 EFFECT OF HIGH SODIUM CONCENTRATIONS ON THE MOBILITY OF CESIUM: ONE-DIMENSIONAL REACTIVE TRANSPORT SIMULATIONS

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D.3.7.1 Introduction

Leaked ¹³⁷Cs has been observed in boreholes at WMA S-SX at depths greater than anticipated based on previous estimates using constant K_d transport models. The depth of penetration of cesium appears to be different depending on the tank waste composition. Tank SX-115 shows little migration of cesium, whereas for tank SX-108 cesium appears to have migrated several tens of meters beneath the tank. It is important to understand what controls the mobility of Cs in the Hanford vadose zone in order to understand the potential hazard Cs could pose to the environment and also to facilitate remediation efforts to clean up the site.

There are several plausible explanations for the observed differences in Cs mobility. One possibility is that competitive sorption effects could enhance the mobility of Cs in the presence of high sodium concentrations. This possibility is considered in more detail in this report. Competition for a limited number of sorption sites between radionuclides and cations in the background electrolyte solution leaked from the tanks could greatly reduce the retardation of cesium. This is consistent with observations in that the fluid leaked from tank SX-115 is much more dilute compared to tank SX-108. Other possibilities include reaction of the tank fluids with the sediments beneath the tanks, thereby altering their sorptive properties, colloid-facilitated transport, and complexing reactions.

In this contribution, the two phase, reactive flow and transport model FLOTRAN (Lichtner 2001) is used to describe the interaction of the leaked tank fluid with host sediments and ambient groundwater in the vadose zone. The effect of high ionic strength fluid leaked from tanks on the mobility of radionuclides is investigated. In this preliminary effort focus is on the radionuclide cesium. A simplified, one-dimensional (1D) model is considered. The model incorporates flow of liquid water, water vapor, air, and heat, in addition to multicomponent reactive chemistry. Both Pitzer and Debye-Hückel activity coefficient algorithms are included in the model calculations. Finally, an estimate of the colloid concentration necessary to affect significantly the mobility of cesium is presented.

D.3.7.2 The K_d Approximation

In an ion exchange process, chromatographic separation takes place between the exchanging cations with distance and time. The extent of separation depends on the affinity of each cation to the exchange surface, the exchange capacity of the medium, and length of time involved. In certain cases it is possible to predict the mobility of each cation based on its distribution coefficient, defined as the ratio of sorbed to aqueous concentration. Cations with larger distribution coefficients move more slowly compared to ones with smaller coefficients. However, in order to use the distribution coefficient approach to estimate mobility, it is necessary that the bulk solution composition remain relatively constant with distance and time.

This requirement is most certainly not met at Hanford for situations in which high ionic strength fluids have leaked from the tanks.

To investigate the dependence of the distribution coefficient on solution composition, exchange of Na and Cs is considered using the three-site sorption model developed by Zachara et al. (2001) for the Hanford sediments. The exchange parameters used in the model are listed in Table D.3.7.1. The distribution coefficient in dimensionless units for the i^{th} cation, valid for monovalent exchange and ignoring complexing, is given by the expression

$$K_i = \frac{(1-\phi)\rho_r}{\phi} \sum_a \left[\frac{Q_a k_i^a}{\sum_l k_l^a c_l} \right] \quad (\text{D.3.7.1})$$

where Q_a refers to the cation exchange capacity of site a , k_i^a is the selectivity coefficient of the i^{th} cation with concentration c_i , sediment particle density is denoted by ρ_r , and porosity by ϕ . The sum is taken over the distinct sorption sites.

Table D.3.7.1. Ion Exchange Parameters for Cs, Na, K, and Ca on Hanford Sediments. Parameters Kindly Provided by Carl Steefel (private communication).

Cation	Log Species Selectivity Coef.		
	Site 1	Site 2	Site 3
Na+	-6.87373	-3.57769	-1.66068
K+	-4.74122	-1.00000	-0.99987
Ca++	-7.52000	-4.58638	-1.50441
Cs+	0.0	0.0	0.0
CEC [mol/kg solid]	2.720e-5	1.3371e-4	7.7844e-2

Plotted in Figure D.3.7.1 along the vertical axis is the logarithm of the retardation factor for Cs, $R=1+K_{Cs}$, against the concentration of Cs and Na along the x- and y-axes, respectively, with the parameter values given in Table D.3.7.1. A porosity of 40% and density of 1.54 g/cm^3 is used in obtaining the retardation. As can be seen from the figure, Cs retardation ranges over four orders of magnitude. Cs becomes more strongly retarded as its own concentration decreases and as the concentration of Na decreases. However, as the concentration of Na increases, Cs mobility as measured by the distribution coefficient rapidly decreases.

Figure D.3.7.1. Retardation Factor for Cs Exchanging with Na on Hanford Sediments.

In the environment of the Hanford tank farms, the concentrations of both Cs and Na were highly variable over time and depth within the vadose zone. Leaks from the tanks took place over relatively short periods of time releasing short duration pulses from weeks to months or years of variable composition tank effluents into the vadose zone. Under such conditions, the mobility of Cs would also have been highly variable. During a pulse release with high Na concentration, Cs mobility could be greatly enhanced. However, because of the slight difference in the Na and Cs distribution coefficients, Cs would still be slightly more retarded compared to Na. As time increased and the leak halted, the chromatographic separation between the Na and Cs plumes would increase. Eventually, given sufficient time and travel distance, the two plumes would become completely separated with cesium left behind in a dilute solution with a greatly reduced mobility. The picture that emerges from this qualitative consideration of the distribution coefficient, is that during the initial release of fluid from the tank, Cs would migrate rapidly as long as it was in the presence of high Na concentrations. But as chromatographic separation set in after the leak had ceased, cesium would become highly retarded. How far Cs could actually migrate through the vadose zone would appear to depend on a number of factors including the leak composition, rate, and duration, surface infiltration rate, and sediment sorptive properties.

D.3.7.3 Model Description

The SX tank farm consists of 15 single-shell tanks with different heat loads (see Sections D.7.1 and D.7.2), some of which have leaked radioactive fluid into the vadose zone. Because of the finite number of tanks and their variable heat loads and the varying positions of suspected leaks from the tanks, it is not possible in a rigorous sense to reduce the size of the problem by symmetry considerations. Nevertheless, to gain insight into the processes taking place within the vadose zone, simplifications are necessary to reduce the system to a manageable size for which relatively rapid simulations can be performed which captures the basic physics and chemistry involved. Use of a 1D model is clearly a gross simplification compared to two- or three-dimensional (2D or 3D) models and therefore should not be considered quantitatively accurate. However, because of the vastly reduced computational effort required for a 1D model

compared to 2D or 3D models, the 1D model allows sensitivity analyses to be more easily performed with incorporation of ~~multiphase-multicomponent~~ chemistry. In what follows 1D simulations are carried out along a vertical column from the ground surface to the water table. Fluid is injected at a depth corresponding to the base of the *tank*. Combined with surface infiltration, the interaction of fluid with sediments is simulated to describe the migration of Cs as it is released from the ~~tank~~. To obtain appropriate leak rates, the model is calibrated against observations from well 299-W23-19, which is located next to *tank* SX-115.

Calculations are performed using the computer code FLOTRAN (Lichtner 2001), a two-phase, multicomponent, reactive flow and transport numerical model. Processes included in the code include two-phase, nonisothermal, flow of mass and heat in variably saturated porous media, and (enhanced) binary diffusion of water vapor and air. The flow equations are coupled to equations describing multicomponent reactive transport through field variables pressure, temperature, liquid and gas velocities, saturation state, and liquid and gas densities. The reactive transport equations account for such processes as aqueous speciation, reactions with minerals, ion exchange and surface complexation, and colloid-facilitated transport. The transport equations, in turn, can be coupled to the flow equations through changes in material properties such as porosity, permeability, tortuosity, and fluid density although this possibility is not considered in the simulations carried out below.

The stratigraphic sequence used in the calculations is listed in Table D.3.7.2. Not included in the present simulations is the possible presence of a thin compacted layer beneath the tanks. The compacted layer has been estimated to be approximately 0.5-1 m thick. However, the physical properties of the compact layer (porosity, permeability, capillary parameters, density) are presently unknown.

Formation	Abbreviations	Thickness [m]
Backfill	BF	16.2
Hanford Fine Sand	HF	23.0
Plio-Pleistocene	PP	6.0
Upper Ringold Gravel	URG	3.0
Middle Ringold	MRG	20.0

Material properties for soil, hydraulic, and thermal parameters used in the calculations are listed in Table D.3.7.3. Parameters α and λ refer to the phenomenological van Genuchten equation relating capillary pressure and saturation. Effective binary gas diffusion is considered with gaseous diffusion constant $D_g^0 = 2.13 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$. Vapor pressure lowering resulting from capillary suction was included in the simulations as described by Kelvin's equation. **An** even more important effect, but not yet incorporated in the simulations, could be the effect of salts on vapor pressure.

Table D.3.7.3. Parameters for Material and Thermal Properties for Intrinsic Rock Density ρ_r , Heat Capacity c , Thermal Conductivity κ , Porosity ϕ , Residual Saturation s_r , van Genuchten Parameters α and λ , and Saturated Permeability k_{sat} .

Formation	ρ_r g/cm ³	c J/kg/K	κ dry W/m/K	κ wet W/m/K	ϕ -	s_r -	α 1/m	λ -	k_{sat} m ²
BF	2.85	800	0.2	2.	0.258	0.077	1.008e-3	0.659	1.24e-12
HF	2.85	800	0.2	2.	0.358	0.084	9.408e-5	0.469	3.37e-13
PP	2.85	800	0.2	2.	0.422	0.259	6.851e-5	0.456	3.73e-14
URG	2.85	800	0.2	2.	0.262	0.213	2.966e-5	0.386	1.44e-13
MRG	2.85	800	0.2	2.	0.164	0.061	6.340e-5	0.392	2.00e-13

D.3.7.4 Calibration to Well 299-W23-19

In this Section, 1D reactive transport simulations are carried out for tank SX-115.

The simulations are based on a simplified chemical system compared to the actual tank composition. Included, in addition to several aqueous complexing reactions, are ion exchange reactions involving cations Cs^+ , Na^+ , K^+ and Ca^{2+} , and precipitation and dissolution of calcite. Results using the Pitzer model are compared with the Debye-Hückel activity coefficient algorithm.

D.3.7.4.1 Model Calibration. Because the geometry of the system is inherently 3D, it is not possible to use the actual leak volumes and rates in 1D simulations. To obtain these parameters for the 1D model, it is necessary to calibrate the model against field observations. Extensive data for concentration of solute species with depth is available from well 299-W23-19, located in the vicinity of tank SX-115 (Serne et al. 2001). The timing of the leak for tank SX-115 is thought to have occurred in 1965, and leak volume and duration are estimated to be 60,000 gallons over a two-week period. The position of the leak is thought to be close to the edge of the tank near the well.

As suggested here, the model parameters for leak rate and duration, average infiltration rate, and solution composition of the leaking fluid are rather tightly constrained by field observations. From the observed profile for NO_3^- , a conservative species that does not take part in exchange, several parameters can be determined. The width of the NO_3^- profile is used to fix the leak duration, and the depth of the peak concentration determines both the infiltration and leak rate. A time span of 35 y is assumed. For the leak rate a value of 8.4×10^{-4} kg/s is obtained, and for the leak duration a value of 1.213×10^6 s, or just over two weeks, in agreement with the estimated value. With these values a total leak volume of 247.6 gallons is released in the 1D model, much smaller than the 60,000 gallons estimated to have leaked. This reduced value is a consequence of neglecting lateral spreading in the 1D model. An infiltration rate of 0.08 m/yr gave the best fit to the nitrate profile. With these values the travel time to the water table for a conservative tracer released from the surface without the tank present is found to be 100 years, and 68 years when released from a depth coinciding with the base of the tank in the presence of the leak.

In addition, the solution composition of the leak can be constrained by the Serne et al. (2001) field data. The concentration of NO_3^- in the leak is adjusted to match the observed peak concentration. Likewise the pH of the leak composition is adjusted to match the observed pH peak at depth. The sodium concentration is determined by charge balance. The initial and source fluid compositions are given in Tables **D.3.7.4** and **D.3.7.5**, respectively. The mineral calcite is allowed to form as a secondary phase, but is assumed not to be present initially.

Initial flow conditions and moisture profile are determined by first running the model without the tank in place at a constant rate of infiltration. An infiltration rate of 8 cm/yr is imposed at the ground surface with a constant temperature of 12.8 °C. At the water table the temperature is fixed at 17 °C. A steady-state profile for moisture content, temperature, and counter flow of vapor and liquid is obtained which is then used with the tank in place. The initial saturation profile is shown in Figure **D.3.7.2** along with profiles at 1 and 10 years following release of fluid from the tank using the material properties and van Genuchten parameters listed in Table **D.3.7.3**. After approximately 10 years the moisture profile has returned to its steady state value. For the 1D model, 136 nodes in the vertical direction are used with equal spacing of 0.5 m. Two zones of elevated moisture content, located at a depth of approximately 43-48 m, coincide with the Plio-Pleistocene and Upper Ringold Gravel stratigraphic units. The water table is located at a depth of approximately 62.4 m. In these preliminary simulations the tank temperature was fixed at 25 °C.

Table D.3.7.4. Initial Fluid Concentration.

solution density = 1.0008 [g/cm³]
 mole fraction H₂O = 9.9960E-01
 activity of water = 9.9962E-01 osmotic coefficient = 9.3347E-01
 pH = 7.5000

species	molality	total	act.	coef.	act.	ratio/H+	constraint
Ca++	2.99733E-03	3.00003E-03	5.84203E-01	1.2354E+01	1	total	
Mg++	2.00000E-03	2.00003E-03	5.8236E-01	1.2178E+01	1	total	
K+	2.67003E-03	2.67000E-03	8.6355E-01	4.8651E+00	1	total	
Na+	9.99993E-04	1.00000E-03	8.6524E-01	4.4385E+00	1	total	
H+	3.6430E-08	2.96553E-05	8.68043E-01	0.0000E+00	8	pH	
NO3-	9.99933E-05	1.00000E-04	8.7227E-01	-1.1439E+01	1	total	
Cl-	1.30073E-02	1.30073E-02	8.8160E-01	-9.3244E+00	-1	chrg	
HC03-	5.5506E-04	5.9304E-04	8.8376E-01	-1.0694E+01	4	CO ₂ (g)	
CS+	1.0000E-16	1.0000E-16	8.5776E-01	-8.5615E+00	1	total	
H ₂ O	5.5508E+01	5.5508E+01	1.0000E+00	1.7444E+00	7	conc	

complex	molality	act.	coef.	act/H+	log K
CO ₂ (aq)	3.39881E-05	1.0022	-4.4687	6.3414	
CaCO ₃ (aq)	2.662003E-06	1.0000	-5.5748	-7.0088	
CO ₃ --	1.329613E-06	0.55218	-20.753	-10.325	
OH-	3.77977E-07	0.85363	-13.861	-13.991	
NaNO ₃ (aq)	6.818953E-09	1.0000	-8.1663	-1.0440	

mineral saturation indices		
mineral	SI	log K
Calcite	-4.20274E-01	-1.85424E+00
Halite	-6.59370E+00	-1.59027E+00
NaNO ₃ (s)	-8.21280E+00	-1.09056E+00

gas	log partial pressure	pressure [bars]	log K
CO ₂ (g)	-3.000	1.0000E-03	7.8092

Table D.3.7.5. Calibrated Source Term Representing the Tank Leak Composition.

solution density	=	1.0638	[g/cm^3]			
mole fraction H2O	=	9.74023-01				
activity of water	=	9.7519E-01	osmotic coefficient =	9.4187E-01		
pH = 10.0000						

species	molality	tot	act.	coef.	act.	ratio/H+ constraint
.....						
Ca++	3.5099E-04	3.58003-04	1.1157E-01	1.6242E+01	1	total
Mg++	1.0000E-04	1.0000E-04	4.1546E-02	1.5696E+01	1	total
K+	1.0000E-03	1.0000E-03	5.12903-01	6.8482E+00	1	total
Na+	7.2778E-01	7.50003-01	6.8217E-01	9.7102E+00	1	total
H+	1.4183E-10	1.1018E-03	7.05083-01	0.0000E+00	8	pH
NO3-	7.26393-01	7.4860E-01	6.8177E-01	-9.9871E+00	-1	chrg
Cl-	1.0000E-03	1.0000E-03	6.3532E-01	-1.2848E+01	1	total
HCO3-	3.5585E-04	1.31053-03	5.1299E-01	-1.3297E+01	3	Calcite
Cs+	1.0000E-04	1.0000E-04	4.07523-01	5.8482E+00	1	total
H2O	5.5508E+01	5.5508E+01	1.0000E+00	1.7444E+00	7	conc

complex	molality	act.	coef.	act/H+	log K	

NaNO3 (aq)	2.221573-02	1.0000		-1.6533	-1.0440	
CO3--	9.47629E-04	9.117473-02		-22.720	-10.325	
OH-	1.472473-04	0.67599		-13.680	-13.991	
CaCO3 (aq)	7.006203-06	1.0000		-5.1545	-7.0088	
CO2 (aq)	3.55139E-08	1.1570		-7.4496	6.3414	

mineral saturation indices						
mineral	SI	log K				

Calcite	0.00000E+00	-1.85424E+00				
NaNO3 (s)	-1.69986E+00	-1.09056E+00				
Halite	-5.09138E+00	-1.59027E+00				

gas	log partial pressure	pressure [bars]	log K			

CO2 (g)	-5.919	1.2063E-06	7.8092			

Figure D.3.7.2. Steady-State Saturation Profile, and Saturation Profiles at 1 and 10 Years Following the Release of Fluid From the Tank. A Constant Infiltration Rate of 8 mm/y is Imposed at the Surface.

D.3.7.4.2 Results. The results of the fit to the Serne (2001) data from well 299-W23-19 are shown in Figure D.3.7.3. Concentration profiles for species NO_3^- , Na^+ , Ca^{2+} , and pH are shown along with field observations from well 299-W23-19 (Serne 2001). While generally speaking the numerical simulation appears to capture the main features of the field data there are some differences. The simulation does not succeed in describing the broad peak in the Na^+ concentration profile, nor does it capture the smaller peak at greater depth. The upper portion of the NO_3^- is not well described either. There is a small displacement between the Na^+ and NO_3^- peaks indicating that Na^+ is slightly retarded. Note that the peak concentrations are less than the source term values by almost a factor of two for nitrate resulting from dilution effects, and roughly a factor of 7.5 for Na^+ resulting from sorption of Na^+ on mineral surfaces as well as dilution. The pH profile was rather remarkably reproduced. The sharp rise in pH (at 21 m) was caused by dissolution of calcite at the leading edge of the zone where secondary calcite formed. The pH gradually decreases as calcite precipitates and begins to increase again as the reaction slows. Calcite disappears and stops reacting at a depth of approximately 47.5 m. The results for the Pitzer and Debye-Hückel activity coefficient algorithms are seen to be quite close to one another.

Figure D.3.7.3. Solute and pH Profiles for an Elapsed Time of 35 Years. Symbols Indicate Experimental Data From Serne (2001). The Symbols P and DH Indicate Pitzer and Debye-Hückel Activity Coefficients, Respectively.

D.3.7.5 Effect of Background Electrolyte Concentration on Cesium Mobility

To investigate the effect of high sodium concentrations on the mobility of cesium, varying source term concentrations of sodium nitrate were used. The injection interval was set at 1 year keeping the total mass of fluid injected the same as in the calibration problem. All other variables were kept fixed to the values used in the calibration problem. Radioactive decay of ^{137}Cs was not taken into account in the calculations. With a half-life of 30.2 years, roughly 300 years are required for ^{137}Cs to decay to negligible levels.

Results of the simulations are presented in Figures D.3.7.4 through D.3.7.8, showing aqueous and sorbed cesium concentrations and aqueous Na concentrations plotted as a function of depth for 35, 50, and 75 years. Sodium concentrations ranged from 0.75 M, corresponding to the calibration problem, to 20 M, which could easily have leaked from tank SX-108 (see Section D.7.3). As is apparent from the figures, with increasing Na^+ concentration, Cs^+ mobility increases. For lower concentrations of Na^+ , however, Cs^+ becomes more retarded compared to Na^+ , resulting in rapid chromatographic separation of the two ions. As a consequence, Cs^+ is left behind in a dilute solution in which it is highly retarded. This is apparent in Figures D.3.7.4, D.3.7.5, and D.3.7.6. However, for more concentrated solutions, it is possible for cesium to penetrate more deeply into the vadose zone as can be seen in Figures D.3.7.7 and D.3.7.8. However, even in these cases Cs^+ began to lag behind Na^+ and becomes more strongly sorbed with depth.

Figure D.3.7.4. Calculated Na and Cs Profiles with Depth for Elapsed Times of 35, 50, and 75 Years for Tank SX-115.

Figure D.3.7.5. Calculated Na and Cs Profiles with Depth for
5 Molal Sodium Nitrate Source Concentration.

Figure D.3.7.6. Calculated Na and Cs Profiles with Depth for
10 Molal Sodium Nitrate Source Concentration.

Figure D.3.7.7. Calculated Na and Cs Profiles with Depth for
15 Molal Sodium Nitrate Source Concentration.

Figure D.3.7.8. Calculated Na and Cs Profiles with Depth for 20 Molal Sodium Nitrate Source Concentration.

The relation between the aqueous and sorbed Cs^+ concentration profiles is noteworthy. As the Na^+ source concentration increases, the sorbed Cs^+ concentration penetrates more deeply into the vadose zone. Near the base of the tank close to the source of the leak, Cs^+ becomes highly retarded once the Na^+ pulse has advanced beyond the injection point. For this reason, Cs^+ is not completely displaced from its point of release. The aqueous Cs^+ concentration rapidly becomes attenuated with depth as more cesium becomes sorbed on the sediments after the Na^+ plume has passed. The sorbed Cs^+ profile formed a quasi-stationary state as time increased and remained in the vadose zone in the presence of dilute ambient groundwater.

Breakthrough curves for 20 M and 25 M sodium nitrate source concentrations are shown in Figure D.3.7.9. A pulse concentration of Cs^+ is released at the water table for these high Na^+ concentrated solutions, which rapidly becomes attenuated with decreasing Na^+ concentration. It should be noted that these results are qualitatively different than would be obtained with a constant K_d description of ion exchange. It was found that Cs^+ mobility is nearly independent of the leak duration over a two week to one year period, provided the source injection rate is scaled so that the same total mass of fluid is injected.

Figure D3.7.9. Cs Breakthrough Curves at the Water Table Corresponding to a Depth of 62.5 m for 20 Molal and 25 Molal Sodium Nitrate Source Concentrations.

D3.7.6 Colloid-Facilitated Transport of Cesium

Another mechanism that could possibly explain the migration of cesium in the vicinity of the tank SX-108 is colloid-facilitated transport. For the case when exchange reactions are fast described by local equilibrium, the effective retardation factor taking into account exchange on colloid and mineral surfaces is given by

$$R_i^{eff} = 1 + \frac{K_i^{min}}{1 + K_i^{coll}} \quad (D.3.7.2)$$

where K_i^{min} and K_i^{coll} refer to the distribution coefficients associated with minerals and colloids, respectively. To obtain this expression it is assumed that colloids and groundwater move at the same average Darcy velocity. From this expression it is apparent that for colloids to appreciably affect radionuclide mobility, the colloid distribution coefficient should be the same order of magnitude as the mineral distribution coefficient or greater. This observation enables an estimate of the colloid concentration necessary to affect cesium mobility.

The distribution coefficient for colloids has a similar form as the distribution coefficient for exchange on mineral surfaces except that in this case it is proportional to the colloid concentration. Thus

$$K_i^{coll} = W_{coll} C_{coll} \sum_{\alpha} \left[\frac{Q_{\alpha}^{coll} k_i^{\alpha}}{\sum_i k_i^{\alpha} c_i} \right] \quad (D.3.7.3)$$

where the colloid concentration is denoted by C_{coll} , W_{coll} refers to the colloid formula weight, and Q_{α}^{coll} the colloid exchange capacity associated with site α . Assuming that exchange on colloids obeys a similar sorption isotherm as on minerals, equating colloid and mineral distribution coefficients yields the following expression for the colloid concentration where a single exchange site is assumed

$$C_{coll} = \frac{\rho_r(1-\phi)Q_{min}}{W_{coll}Q_{coll}} \quad (D.3.7.4)$$

The magnitude of colloid concentration necessary for equal mineral and colloid distribution coefficients, may be obtained by calculating the fraction of the pore volume occupied by colloids. It follows that

$$\phi_{coll} = \frac{W_{coll}C_{coll}}{\rho_{coll}} = \frac{(1-\phi)}{\phi} \frac{\rho_r Q_{min}}{\rho_{coll} Q_{coll}} \cong \frac{1-\phi}{\phi} \quad (D.3.7.5)$$

where ρ_{coll} is the intrinsic colloid density. The latter result is obtained by assuming that the exchange capacities and intrinsic densities for colloids and sediment are similar: $Q_{coll} \approx Q_{min}$, and $\rho_{coll} \approx \rho_{min}$.

According to this result, the entire pore space would be filled with colloids for a porosity of 50% (ρ_{coll}). At lower porosities the condition of equal distribution coefficients is impossible to achieve. This result indicates that a rather large colloid concentration is required if colloids are to compete with minerals for sorption, and thus to affect in a significant way the mobility of cesium. Thus it would appear that a significant influence of colloids on the mobility of cesium can be ruled out, unless cesium is much more strongly sorbed to colloids compared to mineral surfaces in the sediment. It should also be noted, however, that this analysis assumes sorption is reversible. Should sorption on colloids be irreversible, then smaller colloid concentrations could have a significant influence since colloids would not have to compete with minerals in this case.

D.3.7.7 Conclusion and Implications

By utilizing field data from the 299-W23-19 well in the neighborhood of tank SX-I 15, it was possible to calibrate flow parameters and source term to a 1D reactive flow and transport model. The model was then used to analyze the mobility of Cs^+ with varying salinity of the background electrolyte solution used in the source term. It was found that only for very **high** Na^+ concentration was it possible for Cs^+ to advance to the water table. However, the aqueous Cs^+ concentration rapidly became attenuated with depth, **as** more Cs^+ exchanged with the sediments following passage of the Na^+ plume. The sorbed Cs^+ profile formed a quasi-stationary state, remaining in the vadose zone in the presence of dilute ambient groundwater. Finally, it was concluded that colloids under conditions of reversible exchange reactions, are not likely to

provide a feasible mechanism to enhance Cs^+ migration because of the extremely large colloid concentrations that would be required. This conclusion, however, was predicated on the assumption of reversible sorption.

It should be emphasized that the results of numerical simulations presented in this contribution are preliminary in nature. Several possibly important aspects were not included in the simulations reported here. The most obvious is the 1D simplification used in the simulations. **This** was partly corrected for by calibrating the model against field data. However, dilution effects caused by lateral spreading cannot be accounted for in these simulations. In addition, calculations were based on isothermal conditions and did not take into account heat released from the **tanks**. This could be important in accounting for moisture redistribution and effects on chemical interaction. Finally, alteration of surfaces of sorbing minerals by the caustic fluid leaked from the tank was not included in the model.

D.3.7.8 References

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D.3.8 CONCLUSIONS OF S&T INVESTIGATIONS OF CS ADSORPTION AND TRANSPORT IN S-SX SEDIMENTS

$^{137}\text{Cs}^+$ is the radioactive contaminant that has been released to the vadose zone in the highest concentrations in the S and SX tank farms. In-ground inventory estimates developed in other sections of this FIR suggest that 89 kCi or more of $^{137}\text{Cs}^+$ may be sorbed to sediments beneath the S and SX tank farms. Because of its' hard gamma emission and large in-ground concentration, considerable concern exists regarding the future migration of ^{137}Cs . $^{137}\text{Cs}^+$ is also a reference contaminant in the tank farms because it is one of the few radionuclides whose depth distribution can be monitored in-situ by spectral gamma analyses. Often, estimates of the concentration, inventory, and depth penetration of other "gamma invisible" radionuclides (e.g., ^{99}Tc) are derived from the $^{137}\text{Cs}^+$ concentration profile. For these reasons it is important to understand the geochemistry of $^{137}\text{Cs}^+$, and to develop models that describe its i.) distribution between soil and water that determines retardation and transport and ii.) desorption rates from sediment and potential for future migration.

Through study of uncontaminated sediment from the S and SX tank farms ("Above B" composite), we have learned that $^{137}\text{Cs}^+$ adsorbs to Hanford sediment by a highly selective ion exchange process to micas and smectites. The concentration of the adsorption sites is small (10^{-5} mol/g). The highest affinity sites reside on the micas and these are present at 10^{-9} mol/g. While small in concentration, these sites provide a high sorption potential for $^{137}\text{Cs}^+$. The overall extent of adsorption is strongly controlled by Na^+ and Cs^+ concentration as these participate in mass action reactions on the same set of adsorption sites. Na^+ exhibits a strong competitive effect on $^{137}\text{Cs}^+$ adsorption; Na^+ concentrations in excess of 10 mol/L virtually eliminate adsorptive retardation by Hanford sediments. These effects can be described by multi-site, multi-component ion exchange theory and a Cs^+ adsorption model of this type was developed for Hanford sediments that well describes Cs^+ adsorption over the range of Cs^+ and electrolyte concentration found in tank waste. This equilibrium model well described $^{137}\text{Cs}^+$ transport through columns of Hanford sediment at 100% and 64% water saturation under various ionic regimes. In contrast, $^{137}\text{Cs}^+$ transport at 24% water saturation was more rapid than expected (model predicted), because immobile water prevented access of $^{137}\text{Cs}^+$ to high affinity sorption sites. High base interaction with the sediments designed to simulate REDOX waste reactions had minimal effects on $^{137}\text{Cs}^+$ ion exchange adsorption.

Contaminated sediments were studied from boreholes 41-09-39 and SX-108 slant ranging in $^{137}\text{Cs}^+$ content from 10^5 to 10^8 pCi/g. The isotopic composition of exchangeable Cs^+ (^{137}Cs , ^{135}Cs , ^{133}Cs) was measured in these sediments, and ^{137}Cs represented 20.8% of the total Cs pool. ^{137}Cs -containing mineral phases were isolated and identified from a number of core sections with varying distances from the leaked tanks. The ^{137}Cs -containing phases were invariably micas of various types with biotite and weathered biotite giving the highest counts. The high Na^+ in the REDOX wastes had suppressed all ^{137}Cs adsorption except that to the highest affinity sites in the sediment. Desorption studies were performed with four contaminated sediments with different degrees of apparent mineral transformation by waste reaction. The degree of mineral transformation had little discernable impact on the extent or rate of ^{137}Cs desorption. Approximately 30-50% of the adsorbed ^{137}Cs was immediately desorbable (electrolyte dependent) and conformed to predictions from the multi-site Cs^+ exchange model. The remaining sorbed ^{137}Cs pool (50-70%) was not irreversibly sorbed, but was slowly exchangeable

and exhibited a kinetic half-life of 500-1674 days. Electron and X-ray microprobe analyses of Cs^+ -contaminated sediments, and chemical extraction of the same suggested that the poorly exchangeable fraction resided in intra-particle channels (micas) and on sorbent regions coated with secondary mineral precipitates resulting from waste sediment reaction. The desorption behavior was described with a first-order kinetic model that was linked to the equilibrium, multi-site Cs^+ adsorption model.

The multi-site Cs^+ adsorption model was used to predict in-situ ^{137}Cs K_d values for the SX-108 core samples that compared favorably with those measured by water and acid extraction by Serne et al. (2001d). The model was also used in 1D transport simulations to describe ^{137}Cs migration beneath a leaked SX tank where the Na^+ concentration in the REDOX waste was varied as a sensitivity exercise (the Na^+ concentrations of leaked tanks SX-108, SX-109, and SX-115 are not well known). The simulations resulting from a REDOX waste Na^+ concentration of 15-20 mol/L best approximated the in-ground ^{137}Cs distribution. This latter modeling exercise did not include multi-dimensional hydrologic phenomena resulting from fine- and coarse-scale sediment layering that may have influenced or controlled waste migration patterns.

Research in this section has shown that expedited $^{137}\text{Cs}^+$ migration has occurred beneath the S and SX tank farms for at least three chemical reasons: (1) ^{137}Cs migration is very sensitive to Na^+ concentration and the impact of high Na^+ was not taken into account in previous modeling exercises; (2) Na^+ concentrations in leaked REDOX wastes were underestimated in the past; new estimates based on mass balance calculations (D.7.3) and characterization measurements (Serne et al. 2001d) suggest that Na^+ concentrations in SX-108 supernatant may have approached 20 mol/L; and (3) the total concentration of Cs in the supernatant was underestimated because the mass contributions of ^{133}Cs and ^{135}Cs were not accounted for. Physical explanations, such as adsorption site bypass under low water content, and preferential flow paths may also have been at play.

In terms of future behavior, desorption measurements indicate that almost all of the adsorbed ^{137}Cs is exchangeable with the aqueous phase over long contact times, (e.g., > 500 days). Thus, it is available for mobilization and transport if sufficient ionic conditions develop. However, high levels (>5-10 mol/L) of soluble Na^+ would be required to mobilize the adsorbed ^{137}Cs . Because the existing Na^+ plume from REDOX waste lies deeper than ^{137}Cs because of chromatographic separation (Serne et al. 2001d; see also Figures D.3.7.7 and D.3.7.8), conditions are unlikely to develop that will mobilize adsorbed ^{137}Cs unless high salt solutions are released to the vadose zone during tank sluicing. The volume of, and Na^+ concentrations in, sluicing losses should be minimized. The equilibrium multi-site Cs^+ adsorption model and the kinetic desorption model may be used in sensitivity calculations to explore the potential mobilizing effect of sluicing losses of different volumes and compositions.

D.4.0 GEOCHEMISTRY AND REACTIVE TRANSPORT BEHAVIOR OF CHROMIUM

Hexavalent Cr [Cr(VI)] in the form of potassium dichromate was used as an oxidant in the REDOX process to manipulate the valence states of Pu and U. Approximately 50% of the Cr(VI) was reduced in processing; the residual Cr(VI) was discharged to the S and SX tank farms in tank waste. Cr(VI) was soluble in the tank waste and remained in the supernate. The estimated Cr concentration at the time of the leak(s) range from 5.09×10^{-2} mol/L to 4.13×10^{-1} mol/L. While estimates of leak volume (and hence, the mass of Cr) varies depending on the assumptions and inventory estimates, the estimated total mass of Cr lost to the vadose zone from tanks S-104, SX-107, SX-108, SX-109, SX-113, and SX-115 is **2,685 kg** (Jones et al. 2000).

Chromate is, under normal Hanford soil and soil pore water conditions, a mobile anion. For this reason, five or more distinct Cr(VI) plumes exist in the 100 areas that discharge to the Columbia River. This Cr(VI) resulted from the disposal of CrO_4^{2-} , used as a corrosion inhibitor, to the soil surface. Given the high estimated electrolyte concentration and pH of the tank fluids (Section D.7.3), chromate could be even more mobile in the WMA S-SX vadose zone than observed in the 100 Areas. There is only a limited understanding of the behavior of Cr(VI)O_4^{2-} in sediments under conditions as harsh as those imposed by leaking tank fluids. The in-ground inventory of Cr(VI) in the WMA S-SX vadose zone is of concern because of its high mobility and known toxicity. Issues regarding Cr(VI)O_4^{2-} mobility and possible geochemical reactions occurring at the time of the leaks are being investigated under several U.S. DOE EMSP projects. Current concerns, however, center on the potential for in-ground inventories to be remobilized by infiltrating meteoric water or possible spills because of tank waste sluicing.

A series of research activities directed at developing a more complete understanding of Cr geochemistry and reactive transport in sediments influenced by the hyperalkaline, hypersaline tank fluids has been performed and is reported here. Current information on Cr behavior under the extreme conditions suspected during SX tank leaks is inadequate to determine: (1) the rates and extent of Cr reactions at the time of the leaks, (2) the current geochemical status of leaked Cr in the vadose zone, and (3) the susceptibility of WMA S-SX vadose zone Cr to future migration. This new research is ongoing and has involved Hanford S&T Program and EMSP investigators and the use of uncontaminated (B8812) and contaminated (SX-108 slant, 41-09-39) vadose zone sediments. The results and implications of this research are described in the following sections: speciation of chromium in Hanford tank farm SX-108 slant and 41-09-39 core samples determined by X-ray absorption spectroscopy; desorption and leaching of Cr from WMA S-SX sediments; fate and transport of Cr(VI) in Hanford sediments treated with Al-rich, alkaline and saline solutions; and Cr(VI) reduction in homogenous and heterogeneous Fe(II) systems under alkaline conditions at 50 °C.

D.4.1 SPECIATION OF CHROMIUM IN HANFORD TANK FARM SX-108 SLANT AND 41-09-39 CORE SAMPLES DETERMINED BY X-RAY ABSORPTION SPECTROSCOPY

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D.4.1.1 Introduction

Chromium was present in relatively high concentrations in the REDOX tank wastes at WMA S-SX and has been found at concentrations as high as 37,000 ppm in contaminated sediments in the vadose zone beneath SX-108 and SX-109 (Serne et al. 2001a, b). At the high pH values of the tank supernate, aqueous chromium is expected to be dominantly in the chromate (CrO_4^{2-}) form (Baes and Mesmer 1986). This form of chromium is highly mobile in aquatic systems (Richard and Bourg 1991) and acutely toxic (Paschin et al. 1983), teratogenic (Abbasi and Soni 1984), and carcinogenic (Ono 1988). In order to assess the environmental impact of chromium in tank leachates that have been released to the vadose zone, a quantitative knowledge of chromium speciation is essential. More specifically, it must be determined to what extent Cr(VI) species have been reduced, via electron transfer reactions, to Cr(III) species in the sediments in the vadose zone. In contrast to Cr(VI), Cr(III) species should be relatively immobile in Hanford subsurface sediments and of low toxicity to biological organisms.

Although the reduction of Cr(VI) to Cr(III) can occur via both abiotic and biotic pathways (Fendorf et al. 2000), it is likely that abiotic pathways are dominant in the Hanford vadose zone due to the low levels of microorganisms and electron donors present (see Section D.5.1). A possible abiotic pathway is the reaction of Cr(VI) species with the surfaces of Fe(II)-bearing minerals such as magnetite (Fe_3O_4) (Peterson et al. 1996; 1997a) and phyllosilicates such as chlorite and montmorillonite (Brigatti et al. 2000a, b), and biotite and phlogopite (Ilton and Veblen 1994; Ilton et al. 1997). This reaction involves the transfer of an electron from three Fe(II) to one Cr(VI), resulting in Cr(III). Another potential abiotic pathway involves the reaction of aqueous Cr(VI) species with aqueous Fe(II) ions released by the dissolution of Fe(II)-containing minerals (Eary and Rai 1989; Fendorf and Li 1996). Ferrous iron-bearing minerals such as magnetite, ilmenite, biotite, and chlorite are known to occur in WMA S-SX sediments (Section D.1.1), but the extent of Cr(VI) reduction in contaminated areas of the vadose zone is not known. It is possible that such reduction is hindered by the presence of carbonate surface coatings on these Fe(II)-bearing minerals (Doyle et al. 2000) or that the surfaces of

Fe(II)-bearing minerals become quickly passivated early in the Cr(VI) reduction process by the formation of a thin layer of amorphous Cr(III)-oxyhydroxide (Peterson et al. 1997b; Kendelewicz et al. 2000; Brown et al. 2000). The presence of significant percentages of Cr(VI) relative to total Cr in the vadose zone sediments, as discussed below, suggests that the inorganic and organic reductants present are not capable of reducing the quantities of Cr(VI) that have been introduced or that the reduction process is in some way inhibited.

In order to determine the relative concentration of Cr(VI) vs. Cr(III) in representative samples from contaminated zones beneath the Hanford tank farm, we carried out a detailed synchrotron-based X-ray absorption fine structure (XAFS) spectroscopy study of eight subsurface samples from the Hanford SX tank farm – six from the SX-108 slant borehole (samples SX-108-6A, -7A, -8A, -9A, -13A, and -14A) and two from borehole 41-09-39 (samples 41-09-39-6AB and 41-09-39-7ABC). The concentrations of chromium in these samples (in mg Cr/g sediment), as determined by x-ray fluorescence analysis are 1186 (41-09-39-6AB, 2090 (41-09-39-7ABC), 955 (SX-108-6A), 1297 (SX-108-7A), 2098 (SX-108-8A), 1394 (SX-108-9A), 931 (SX-108-13A), and 565 (SX-108-14A).

At these concentration levels, the technique of choice for determining the relative proportions of Cr(VI) vs. Cr(III) in mineralogically complex samples of this type is XAFS spectroscopy, which is element-selective, nondestructive, requires no significant sample preparation, and can be measured under ambient conditions (Brown et al. 1988). The basic XAFS experiment involves exposure of a powdered sample or thin section to a very intense monochromatic beam of x-rays from a synchrotron source. The energy of the x-ray beam is varied in steps using a crystal monochromator over a selected energy range that typically begins 20 to 30 eV below the absorption edge of the element of interest and increases to several hundred eV above the absorption edge. The energy steps used vary from several tenths of an eV to several eV. When the energy of the incident x-ray beam matches the energy with which core-level electrons (e.g., 1s) are held, core electrons are excited to valence or continuum levels, in which case they are scattered by atoms surrounding the excited atom. This excitation process results in the absorption of x-rays, and there is a corresponding steep rise in x-ray absorbance at this energy in the absorbance vs. incident x-ray energy spectrum. The fine structure in the spectrum above the absorption edge is due to the constructive and destructive interference of photoelectron waves as photoelectrons are scattered among the neighboring atoms around the absorbing atom. When the neighboring atoms around an absorbing atom such as Cr differ in number or in distances from the central absorber in two different samples, the resulting x-ray absorption fine structure spectra will exhibit significant differences that can be analyzed to quantify these structural differences.

The absorption edge position shifts to higher energy with increasing oxidation state of an element. In the case of chromium, for example, the inflection point of the absorption edge of Cr(III) occurs at ≈ 5998 eV and that of Cr(VI) occurs at ≈ 6005 eV. However, a more sensitive indicator of Cr(VI) vs. Cr(III) is a “pre-edge” feature that occurs at ≈ 5993 eV and varies in intensity depending on the Cr(VI):Cr(III) ratio. The dipole matrix elements that govern the probability of the $1s \rightarrow 3d$ electronic transitions responsible for the pre-edge feature indicate that the probability of this transition should be greatest when Cr(VI) is coordinated by four oxygens in approximate T_d point symmetry, resulting in the highest integrated intensity and height of the pre-edge feature. In contrast, Cr(III) is coordinated by six oxygens in approximate O_h point symmetry, and the probability of $1s \rightarrow 3d$ electronic transitions is low for this coordination

geometry, resulting in a much smaller integrated intensity and height of the pre-edge feature. One can calibrate the variation in pre-edge intensity or height as a function of the Cr(VI):Cr(III) ratio in a series of samples prepared by mechanically mixing known proportions of Cr(VI)-containing and Cr(III)-containing minerals. Such a calibration is shown in Figure D.4.1.1.

Figure D.4.1.1. Cr Pre-edge Height Calibration for Beamline 11-2 at the Stanford Synchrotron Radiation Laboratory: (left) Variation of Pre-Edge Peak Height of Cr K-Edge XANES Spectra as a Function of Cr(VI)/Total Cr. (right) Plot of Cr(VI)/Total Cr versus Cr Pre-Edge Peak Height (from Peterson 1996).

By measuring the XANES (x-ray absorption near-edge structure) spectra of the four Hanford S and SX tank farms borehole samples on the new Molecular Environmental Science beam line (11-2) at the Stanford Synchrotron Radiation Laboratory (Bargar et al. 2001), or on the general XAFS beamline (4-3), and using a calibration curve of the type described above, we determined quantitatively the Cr(VI):Cr(III) ratios of these samples. The results of this study are reported below.

In a separate series of experiments, we examined the spatial distribution of Cr(VI) and Cr(III) species in thin sections of four of the Hanford tank farm borehole samples prepared at PNNL using a highly focused beam of x-rays. This method is known as x-ray micro-fluorescence elemental mapping and was accomplished on the undulator beam line at GSECARS Sector 13 (Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois). Using a $10\mu\text{m} \times 10\mu\text{m}$ x-ray beam tuned to an energy just above the Fe K-absorption edge (7,112 eV), we mapped K, Ca, Ti, Cr, Fe, and Mn in $300\mu\text{m} \times 300\mu\text{m}$ areas on the four thin sections. In separate experiments, we also measured Cr K-edge micro-XANES spectra of a number of points on these thin sections to determine Cr speciation. Bulk Cr K-edge XANES spectra of the thin sections were collected at the Stanford Synchrotron Radiation Laboratory to evaluate the effects of sample preparation on the Cr speciation in the thin sections. The results of these experiments are reported below.

D.4.1.2 Chromium XANES Spectroscopic Analyses of Untreated Samples

D.4.1.2.1 Experimental Procedure. Contaminated sediment samples from the Hanford S and SX tank farms boreholes described above were packed in doubly contained sample holders and shipped from PNNL to the Stanford Linear Accelerator Center for XAFS analysis. The radiation levels of 0.25 g portions of the four powdered samples were as follows: 41-09-39-7ABC (1.7×10^7 pCi/g ^{137}Cs + 1160 pCi/g ^{99}Tc); 41-09-39-6AB (1.1×10^4 pCi/g ^{137}Cs + 3586 pCi/g ^{99}Tc); SX-108-6A (5.3×10^7 pCi/g ^{137}Cs + 77.8 pCi/g ^{99}Tc); SX-108-7A (2.1×10^7 pCi/g ^{137}Cs + 1160 pCi/g ^{99}Tc); SX-108-08A (5.5×10^5 pCi/g ^{137}Cs + 2116 pCi/g ^{99}Tc); SX-108-9A (171 pCi/g ^{137}Cs + 4240 pCi/g ^{99}Tc); SX-108-13A (440 pCi/g ^{137}Cs + 7500 pCi/g ^{99}Tc); SX-108-14A (837 pCi/g ^{137}Cs + 7510 pCi/g ^{99}Tc). The volume of each sample examined was approximately $15\text{ mm} \times 2\text{ mm} \times 1\text{ mm}$ (the volume illuminated by the x-ray beam at SSRL) and the bulk density of each sample was approximately 1.6 g/cm^3 . These samples were held in Teflon sample holders with 10 mil Mylar windows and were sequentially placed in a sample positioner for XAFS experiments. An Ar-filled Stern-Heald-type x-ray fluorescence detector (Lytle et al. 1984) or a 13-element Ge detector was used to monitor Cr K α fluorescence as a function of incident x-ray energy. A 3 px-thickness V filter was placed between the sample and the detector to minimize scattering and thus reduce background radiation. The sample container was purged with He prior to data collection, and He was flowed through the sample container during data collection to minimize air scatter.

Cr K-XANES spectra were measured on the Molecular Environmental Science Beam Line (BL 11-2) (Bargar et al. 2001) or a general XAFS beamline (BL 4-3) over the energy range 5900 eV to 6350 eV using a Si (220) double-crystal monochromator (cryogenically cooled on BL 11-2), with the SPEAR ring operating at 80 to 100 mA electron current and 3 GeV energy. The vertical slit before the monochromator was adjusted to 1 mm height to maximize energy

resolution. A step size of 0.15 eV was used in the energy region 5980 to 6010 eV, and a step size of 1 eV was used over the energy region 6010 to 6350 eV. An integration time of 4 seconds was used at each step. Because the samples were too thick (2 mm), it was not possible to simultaneously collect x-ray fluorescence data from the sample and transmission data from a Cr metal foil used for energy calibration. However, foil edges were collected within 40 minutes of XANES measurements for each sample, and the drift of the monochromator was found to be negligible during this time frame. The first inflection point of the Cr metal foil edge was set to 5989 eV. The deviation from this value was recorded (it was typically around 0.3 to 0.5 eV too small), and the sample spectra were calibrated in energy using this inflection point energy value. Two scans of each sample were recorded and averaged as described below. Reduction of REDOX-sensitive elements like Cr can occur in the intense x-ray beam of a synchrotron and must be monitored in these types of experiments. No evidence of beam-induced Cr(VI) to Cr(III) reduction was observed over the relatively short time exposures (15 to 20 minutes) necessary to collect the Cr K-XANES spectra on the eight Hanford S and SX tank farms borehole samples.

D.4.1.2.2 Data Analysis and Results. The methods of Peterson et al. (1997a) were used to analyze the Cr(VI) content of the Hanford borehole samples. The sample data (typically two scans) were averaged using the computer code MAVE, which is a subroutine in the XAFS data analysis package EXAFSPAK (George and Pickering 1993). No dead time corrections were made. The peak of the pre-edge feature was selected as the calibration point in the EXAFSPAK subroutine MCALIB, as this feature's position should not have changed during the experiment. The position observed was then shifted by the amount of offset measured in the Cr foil (for example, if the feature occurred at 5992.86 eV, and the Cr foil edge was 0.38 eV too low, the data were shifted by + 0.38 eV, resulting in a pre-edge position of 5993.24 eV). The average pre-edge peak position for all eight samples was found to be 5993.3 ± 0.1 eV (see Table D.4.1.1).

Table D.4.1.1. Results of Cr(VI) Determination From XAFS “Pre-Edge” Heights.

Sample	SSRL Beamline	Pre-edge Position (eV)	Normalized Pre-edge Height	% Cr(VI)
41-09-39-6AB	11-2	5993.2 ± 0.1	0.624	51
41-09-39-7ABC	11-2	5993.2 ± 0.1	0.684	58
SX-108-6A	4-3	5993.3 ± 0.1	0.520	54
SX-108-7A	11-2	5993.2 ± 0.1	0.367	25
SX-108-9A	4-3	5993.3 ± 0.1	0.653	71
SX-108-13A	4-3	5993.3 ± 0.1	0.635	69
SX-108-14A	4-3	5993.3 ± 0.1	0.583	62

The averaged data were then analyzed using the EXAFSPAK subroutine PROCESS by background subtraction using a polynomial pre-edge fit of the data up to 5960 eV. A spline was

then fit to the data from 6005 eV to the end of the data (approximately 6350 eV). A third-order spline with two regions was used to fit this region of the spectrum, with a k^4 weighting. The normalization point for the edgejump was set at 6025 eV. The data were normalized on the 6025 eV spline point and output into an ASCII format. The pre-edge features of these normalized spectra were then analyzed using the program Grams/32, where a maximum search was performed, yielding the pre-edge peak height and position. The percent Cr(VI) was then calculated using these peak height values and the equations below from beamline-specific calibration curves:

$$\text{BL 11-2: \%Cr(VI)} = 102.83(\text{height}) - 12.80$$

$$\text{BL 4-3: \%Cr(VI)} = 128.64(\text{height}) - 12.77$$

A plot of the beamline 11-2 calibration curve with the Cr(VI) percentage 95% prediction intervals is shown in Figure D.4.1.1. The prediction interval includes, with 95% confidence, any future Cr(VI) percentages calculated from the Cr pre-edge peak height using the above linear regression equation. The calibration curve properly predicted the Cr(VI) percentages of three unknown samples that were used to test the calibration process.

The normalized Cr K-XANES spectra of the eight Hanford borehole samples are shown in Figure D.4.1.2, and the results of the Cr(VI) determination are shown in Table D.4.1.1.

D.4.1.3 Chromium Speciation Mapping and Micro-XANES Spectroscopic Analyses of Thin Sections

D.4.1.3.1 Experimental Procedure and Data Analysis. We examined four subsurface samples obtained from the Hanford S and SX tank farms using XAFS spectroscopy and X-ray microprobe elemental mapping at the Advanced Photon Source (GeoSoilEnviroCARS Sector 13; Newville et al. 1999). These consisted of different portions of the same two samples from the SX-108 slant borehole (samples SX-108-7A and SX-108-8A) and the same two samples from borehole 41-09-39 (samples 41-09-39-6AB and 41-09-39-7ABC) that were examined at SSRL. Prior to examination, these samples were placed in an Al-tube and impregnated with epoxy at PNNL. Once the epoxy had hardened, the samples were cut in cross section and polished to produce 0.1-mm-thick wafers. Each wafer was glued to a SiO₂-glass plate, sealed with Kapton™ film, and sent to the Advanced Photon Source (APS) for micro-XRF and micro-XAFS analysis. Once at the APS, the samples were placed into acrylic sample holders and sealed with a second Kapton™ film.

This undulator-based instrument uses a Si(111) cryogenic, double-crystal, scannable monochromator. The x-ray micro-beam was produced using Kirkpatrick-Baez (KB) micro-focusing mirrors (Eng et al. 1999). The KB system consisted of two mirrors (100 mm length), one in the horizontal plane and one in the vertical plane, which focused the x-ray beam from 350 μm down to approximately 5 pm. The mirrors are made of single-crystal silicon coated with several hundred Å of Rh, and the flat surfaces were dynamically bent to elliptical shapes using mechanical benders. The “double-bounce” focusing system provided excellent harmonic rejection capabilities for micro-XAFS applications. Samples were placed on an x-y-z stepping motor stage (0.1 μm resolution, positioned at 45° to the incident beam) allowing the

analysis point of interest to be positioned in the monochromatic x-ray beam. An optical microscope, consisting of a 5x Mitutoya, long-working-distance objective lens mounted to an Optem motor-driven focus/zoom transport tube and equipped with a CCD camera, was used to view the samples at high resolution. The position of the x-ray beam was determined using a luminescent phosphor (YAG) mounted to the sample stage. The position stability of the beam on the sample was of the order 0.1°m . Micro-XRF and micro x-ray absorption fine structure (XAFS) spectra were collected in fluorescence mode using a 16-element Ge solid-state detector (Canberra) positioned at 90° to the incident beam and in the horizontal, polarization plane of the synchrotron (position of minimum scattered background radiation). The electron current of the APS storage ring ranged from 60 to 100 mA at an energy of 7 GeV.

Initially, x-ray fluorescence spectra were collected on representative areas of the four core samples. Each sample was moved through the beam over a $300\ \mu\text{m} \times 300\ \mu\text{m}$ area in $10\ \mu\text{m}$ steps, in order to determine the elemental associations of Fe, Cr, Mn, K, Ca, and Ti. XANES spectra were collected at the Cr K-edge on selected spots in each sample and along linear transects of each sample. In general, high Cr spots were selected for single analysis spots, but the line scans also sampled lower Cr material. XANES spectra were also collected from the model compounds, Na_2CrO_4 , BaCrO_4 , and $\text{Na}_2\text{Cr}_2\text{O}_7$. Additionally, the focused beam **was** kept on the Cr(VI)-containing models and on Cr(VI)-rich regions of the samples for 1 hour to evaluate the potential for x-ray-induced reduction of Cr(VI). No such reduction was observed in this time frame.

The fraction of total Cr present as Cr(VI) in each sample spot was determined by comparing the area of the pre-edge peak for the unknown samples to that of Na_2CrO_4 and BaCrO_4 . The Cr XANES spectra were normalized to an edge jump defined by the difference of pre-edge background and the height of the spline at 6030 eV as described above (Peterson et al. 1997a) (Figure D.4.1.5). The area of the pre-edge peak was determined by fitting this peak with mixed Gaussian and Lorentzian functions using the program Grams/32.

D.4.1.4 Results

The spatial distribution of each element within each sample was found to be highly heterogeneous even in an area as small as $300\ \mu\text{m} \times 300\ \mu\text{m}$. Figure D.4.1.3 shows the element maps of two samples as examples. Qualitative correlations between certain elements are visible in the maps (e.g., Cr and Mn from Figure D.4.1.3a). Using the data provided from the element maps for the four samples, scatter plots (Figure D.4.1.4) were generated to further investigate the elemental associations. While sample 41-09-39-6AB shows a moderately strong association between chromium and both manganese and iron, the other samples show a weaker correlation. Samples SX-108-07A, 41-09-39-7ABC, and SX-108-8A (shown in Figure D.4.1.4) have weak linear associations, and the shape of their scatter plots suggests a possible weak quadratic association. A filter was applied to the chromium matrix in order to look for correlations with other elements at spatial positions where there are high chromium concentrations (greater than 75th quantile) and low chromium concentrations (less than 25th quantile). This data treatment did not significantly improve the correlations between chromium and any other element. Plotting some of the data using a quadratic relationship also showed no significant improvement in the correlation between chemical elements.

Figure D.4.1.2. Normalized Cr K-Edge XANES Spectra of the SX-108 Contaminated Sediment Samples: (a) 41-09-39-6AB, (b) 41-09-39-7ABC, (c) SX-108-6A, (d) SX-108-7A, (e) SX-108-8A, (f) SX-108-9A, (g) SX-108-13A, (h) SX-108-14A.

Figure D.4.1.3. Element Maps of Selected Areas From a) Sample 41-09-39-6AB and b) Sample SX-108-8A.

Note: Total Dimensions of the Scanned Image are $300\mu\text{m} \times 300\mu\text{m}$ and Each Pixel Element is $10\mu\text{m} \times 10\mu\text{m}$. Light Areas Have the Highest Concentrations and Dark Areas Have the Lowest.

Figure D.4.1.4. Scatter Plots Between Cr, Mn, Fe, and Ti for Sample SX-108-8A.

Note: The Plots in the Same Row as the Elements have that Element's Normalized Fluorescence Intensity Plotted Along the x-Axis. The y-Axis of That Plot Corresponds to the Element in the Column.

Figure D.4.1.5. Selected Cr K-XANES Spectra Collected From Sample SX-108-8A. Normalized Absorbance is Plotted on the Vertical Axis.

Correlation coefficients were calculated in order to estimate the linear dependence between pairs of elements in the samples. The log correlation matrices for the four samples are shown in Table D.4.1.2. As expected there is a strong association between manganese and iron in all of the core samples and a very weak association between calcium and all other elements except potassium. Sample 41-09-39-6AB also shows a strong correlation between chromium and manganese (0.94) and iron (0.81). However, this strong association with chromium is not repeated in the other samples, with their correlation coefficients ranging between 0.46 and 0.60 for manganese and between 0.32 and 0.59 for iron. The correlation coefficient for chromium and titanium ranged from 0.29 to 0.58 for the four samples. The lack of strong correlations between Cr, Fe, and Mn suggests that sorption reactions between Cr and Fe- or Mn-oxide particles are limited. There is also evidence that such reactions occur to varying degrees in the samples.

The analyses of Cr micro-XANES spectra taken at 53 spots on the four thin sections yielded average Cr(VI) percentages of 13%, 28%, 23%, and 12% for SX-108-7A, SX-108-8A, 41-09-39-6AB, and 41-09-39-7ABC, respectively (Table D.4.1.3). All spots analyzed but two contained mixtures of Cr(III) and Cr(IV). Of the two end member spots, one was Cr(III) and the other was Cr(VI). These results indicate that, in general, the two species are intermixed at the 10 μm scale (approximate analysis scale).

**Table D.4.1.2. Log Correlation Matrices for Ca, Cr, Fe, K, Mn,
and Ti in the Four Core Sample Thin Sections.**

Sample 41-09-39-6AB						
	Ca	Cr	Fe	K	Mn	Ti
Ca	1.00	-0.30	-0.32	0.65	-0.29	-0.22
Cr	-0.30	1.00	0.81	0.16	0.94	0.58
Fe	-0.32	0.81	1.00	0.16	0.86	0.54
K	0.65	0.16	0.16	1.00	0.16	0.23
Mn	-0.29	0.94	0.86	0.16	1.00	0.58
Ti	-0.22	0.58	0.54	0.23	0.58	1.00
Sample 41-09-39-7ABC						
	Ca	Cr	Fe	K	Mn	Ti
Ca	1.00	-0.02	0.15	0.83	0.17	0.02
Cr	-0.02	1.00	0.32	0.13	0.46	0.29
Fe	0.15	0.32	1.00	0.27	0.96	0.66
K	0.83	0.13	0.27	1.00	0.29	0.34
Mn	0.17	0.46	0.96	0.29	1.00	0.64
Ti	0.02	0.29	0.66	0.34	0.64	1.00
Sample SX108-07A						
	Ca	Cr	Fe	K	Mn	Ti
Ca	1.00	-0.16	-0.30	0.75	-0.14	0.03
Cr	-0.16	1.00	0.53	0.04	0.56	0.31
Fe	-0.30	0.53	1.00	-0.14	0.83	0.24
K	0.75	0.04	-0.14	1.00	-0.04	0.34
Mn	-0.14	0.56	0.83	-0.04	1.00	0.19
Ti	0.03	0.31	0.24	0.34	0.19	1.00
Sample SX-108-8A						
	Ca	Cr	Fe	K	Mn	Ti
Ca	1.00	0.31	0.34	0.38	0.36	0.31
Cr	0.31	1.00	0.59	0.09	0.60	0.58
Fe	0.34	0.59	1.00	0.11	0.90	0.54
K	0.38	0.09	0.11	1.00	0.07	0.38
Mn	0.36	0.60	0.90	0.07	1.00	0.43
Ti	0.31	0.58	0.54	0.38	0.43	1.00

Table D.4.1.3. Percent of Total Cr as Cr(VI) From Micro-XANES Analysis.

Core SX-108	Sample Spot*	Cr(VI) content (%)	Core 41-09-39	Sample Spot*	Cr(VI) content (%)
SX-108-07A			41-09-39-6AB		
	1	1		1	22
	2	12		2	6
	3	25		4	35
	L1	17		5	38
	L2	24		6	39
	L3	8		8	43
	L4	10		10	17
	L5	8		12	10
	L6	11		13	20
	L7	11		L1	14
		Avg. = 13		L2	16
				L3	17
SX-108-08A				L4	28
	1	20			Avg. = 23
	2	11			
	3	6	41-09-39-7ABC		
	4	27		1	10
	5	42		2	10
	6	46		3	17
	7	48		L1	8
	L1	16		L2	12
	L2	14		L3	17
	L3	18		L4	11
	L4	15		L5	11
	L5	16		L6	10
	L6	19		L7	13
	L7	24		L8	10
	L8	25		L9	9
	L9	100		L10	11
		Avg. = 28		L11	12
					Avg. = 12

*XANES spectra collected from 10 μm x 10 μm spots. Data from regions with an "L" designation were collected during a "line-scan" across a Cr-rich region of each sample.

Thus, the micro-XANES results showed more reduced chromium than the bulk XANES measurements. The cause of this difference is not fully understood but there are several possible explanations. One possibility is that the original sample aliquots had different oxidation states, but this seems unlikely since the samples were derived from the same parent material. The fact that all four sectioned samples yielded more reduced Cr suggests that Cr reduction may have occurred subsequent to borehole sampling. Reduction of Cr(VI) by the x-ray beam was ruled out – changes in redox state were not observed for the model compounds or in sample regions that were illuminated for up to 1 hour. Thus, photochemical reduction of Cr(VI) was negligible over the time scales of the XANES measurements. Another possibility is that the thin section preparation process, involving epoxy impregnation, slicing, and grinding, may have resulted in Cr reduction.

To investigate possible redox changes introduced by thin section preparation, we epoxy-impregnated Na_2CrO_4 and measured Cr K XANES spectra on beam line 4-3 at the Stanford Synchrotron Radiation Laboratory. These Cr K-XANES spectra showed no Cr(III) suggesting that the Cr oxidation state is unaltered by the epoxy used in sample preparation (although admittedly, there may be significant differences in the behavior of the model compound and the soils during such treatment). To further evaluate possible Cr reduction due to thin section preparation, bulk XANES measurements were carried out on two of the thin sections (41-09-39-6AB and 41-09-39-7ABC) and two thin sections adjacent in the core to those analyzed at the APS (SX-108-7B and SX-108-8B) on beamline 4-3 at SSRL. The procedures used were identical to those described in Section II. The bulk XANES of the thin sections showed a good agreement with the micro-XANES measurement of the Cr(VI) content of the samples, and both showed significant deviation from the bulk XANES of the untreated samples (Table D.4.1.4). These results suggest that the method of thin section preparation employed caused a significant decrease in the Cr(VI):Cr(III) ratio in the samples. A number of scenarios during thin section preparation could have caused this decrease, including epoxy replacement of Cr(VI)-bearing porewater, epoxy-induced dissolution and mobilization of Fe(II) from Fe(II)-bearing minerals, causing Cr(VI) reduction by Fe(II), or direct reduction of Cr(VI) by the epoxy. While no direct reduction of Cr(VI) in solid Na_2CrO_4 by the epoxy was observed, as noted above, Cr(VI) in the samples would occur (presumably) as aqueous, adsorbed, or possibly precipitated CrO_4^{2-} . The prior two forms may show a much higher propensity for reduction by epoxy than the solid form.

Sample	%Cr(VI) from bulk XANES	%Cr(VI) from micro-XANES of thin section	%Cr(VI) from bulk XANES of thin section
41-09-39-6AB	51	23	36
41-09-39-7ABC	58	12	9
SX-108-7B	25	13	11
SX-108-8B	53	28	16

D.4.1.5 Conclusions

Seven of the eight samples from boreholes drilled at the Hanford S and SX tank farms contain 51-71% Cr(VI), whereas the fourth sample (SX-108-7B) contains 25% Cr(VI). These data suggest that while significant reduction of chromium has occurred, most likely via abiotic pathways due to the lack of significant numbers of microorganisms in the Hanford vadose zone, it has not been complete, assuming that the bulk of Cr introduced into the Hanford vadose zone was Cr(VI). Possible reasons for this include (1) insufficient reductants in the vadose zone, (2) the presence of nonconductive carbonate coatings on Fe(II)-bearing minerals, (3) the build-up of nonconducting Cr(III)-hydroxide coatings on reductant surfaces, which can quickly stop the electron transfer process necessary for the Cr(VI) to Cr(III) reduction reaction, or (4) some other process that has inhibited the transfer of electrons from reductants to Cr(VI).

Micro-fluorescence elemental mapping of Cr, Fe, Mn, Ti, Ca, and K at $10\mu\text{m} \times 10\mu\text{m}$ spatial resolution in $300\mu\text{m} \times 300\mu\text{m}$ areas on thin sections of four of the borehole samples showed that they are highly heterogeneous with respect to these elements, with Cr(III) hot-spots (diameters of several $100\mu\text{m}^2$) occurring, presumably as a result of the precipitation of Cr(III)-hydroxides or chromite or sorption of Cr on Fe(III)-hydroxides. Trivalent and hexavalent chromium are intermixed on a very fine scale (less than $10\mu\text{m}$). The spatial correlation between Cr and Fe-bearing minerals, which are likely reductants for Cr(VI), is strong in only one of the four thin sections, indicating that such reactions are limited and occur to varying degrees in these materials.

A comparison of the Cr speciation data from the bulk XANES analysis of the untreated samples and thin sections conducted at SSRL and the micro-XANES analysis of the thin sections conducted at the APS indicates major differences in Cr(VI) concentrations, with the thin section results showing average Cr(VI) percentages of 9-36%. We conclude, however, that the untreated sample results are more representative of the true average Cr speciation in the eight borehole samples examined. This conclusion is based on the significant differences in the Cr(VI):Cr(III) ratios between the untreated samples and the thin sections.

D.4.1.6 Acknowledgments

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D.4.1.7 References

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D.4.2 DESORPTION AND LEACHING OF CR FROM WMA S-SX SEDIMENTS

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D.4.2.1 Introduction

Hexavalent chromium [chromate; Cr(VI)O_4^{2-}] is a highly mobile contaminant in the unconfined aquifer underlying the Hanford reservation. The retardation of Cr(VI), in the absence of reduction to the more stable Cr(III) species, has been shown to result from interactions at mineral-water interface (Ainsworth et al. 1989; Zachara et al. 1989). This interaction is dependent on a number of factors: (1) the nature of the surface (surface charge and its variation with pH, number of sorption sites etc.), (2) the presence of grain coatings, (3) the pH and ionic strength of aqueous phase in contact with geologic material, (4) the mode of adsorption (inner-sphere vs. outer-sphere), and (5) the effect of other surface complexants (Brown et al. 1998). As an anion, Cr(VI)O_4^{2-} will sorb most strongly within the pH range below a sorbent's point of net zero charge where the surface is positively charged; for most Fe oxide minerals that means slightly basic to acidic conditions (Cornell and Schwertmann 1996). Because of the slightly basic pH of Hanford groundwater, chromate is not expected to be substantially retarded; in fact, it is considered a highly mobile species.

The sediments directly below the WMA S-SX and above groundwater consist primarily of the Hanford formation. These sediments (Pleistocene-age flood deposits) are a complex association of mineral phases, including unstable primary phases (e.g., feldspars, micas, etc.), and more stable secondary phases (e.g., Al and Fe oxides, poorly crystalline SiO_2 , and smectites). Because of the harsh nature of tank leaked fluids (high base, high Na concentrations, etc.) from the SX tanks. Sediments inundated by these fluids may have undergone substantial dissolution and precipitation of secondary mineral phases (see Section D.2.0). Chromate associated with these leak events has moved into the vadose zone in significant concentration (Jones et al. 2000). Chromate interactions with Hanford sediments are being studied as part of groundwater transport studies, remedial actions, and demonstrations, but there is only a limited understanding of chromate behavior in contaminated WMA S-SX sediments.

Here we report on new studies of Cr desorption from WMA S-SX sediments under tank SX-108 (SX-108 slant borehole and 41-09-39). These studies investigated Cr desorption in batch and small columns designed to address two main issues. First, the high pH and NaNO_3 concentrations associated with the leaked materials should enhance the Cr(VI) anion's mobility in the affected sediments. Second, accelerated weathering of minerals should cause substantial secondary oxide formation capable of retarding Cr(VI) mobility. These two issues are fundamentally opposing views. By investigating the mobility of Cr(VI) using contaminated sediments and in conjunction with other, linked studies a more complete understanding will evolve regarding Cr behavior below the WMA S-SX.

D.4.2.2 Experimental Procedures

D.4.2.2.1 Sediment Collection and Analysis. Collection and preliminary analyses of sediments from the SX-108 slant and 41-09-39 boreholes are discussed elsewhere (Serne et al. 2001a, b). Materials used in these investigations were SX-108 sediments 7A and 8A and 41-09-39 sediments 6AB and 7ABC. Subsamples of the field moist material were air-dried to a constant weight and sieved to pass a 2 mm mesh. Gravels greater than 2 mm were removed from the air-dried material during the sieving process. The sieved material was thoroughly mixed to obtain a homogeneous sample. Total chemical composition of triplicate subsamples of the homogenized, dried sediments was determined by X-ray fluorescence spectroscopy (XRF). Chromium speciation [Cr(VI)/Cr(III)] in the aforementioned sediments was determined by X-ray absorption spectroscopy (XAS); sample preparation and procedures of these measurements are described elsewhere (Section D.4.1).

D.4.2.2.2 Time-Dependent Cr Desorption with Ammonium Oxalate $(\text{NH}_4)_2\text{C}_2\text{O}_4$.

Batch-type desorption experiments were performed in duplicate by suspending approximately 0.5 g of sediment (SX-108 7A and 41-09-39 7ABC) in 5 g of 0.25 mol/L $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in Oak Ridge centrifuge tubes. Tubes were sealed and agitated at 25 °C. At prescribed time intervals (0.1, 0.4, 2, 8, 32, and 64 days) tubes were centrifuged (5000 rcf for 30 minutes). The supernate was carefully transferred to a plastic syringe fitted with a 0.2 µm filter. The first 1-mL of filtrate was discarded and the remaining filtrate collected in a plastic tube. The filtrate was analyzed for metals of interest (e.g., Fe, Al, Ba, Ca, Cr, K, Mg, Na, and Si) using ICP-OES.

D.4.2.2.3 Cr Leaching from Columns. Two sets of column experiments were conducted to determine Cr(VI) release from WMA S-SX sediments. Approximately 2g of air-dried sediments from each sample (SX-108 7A, SX-108 8A, 41-09-39 6AB, and 41-09-39 7ABC) were packed into 3.1 cm length by 0.78 cm diameter polypropylene columns. The columns were then connected to a peristaltic pump on one side and a fraction collector on the other. Before columns were connected to a leaching solution, approximately 10mL pure CO₂ gas was injected through the columns to displace air from sediment pore space. A uniform movement of the leaching solution through the packed air-dried sediments was observed.

In the first leaching experiment, the sediments were continually leached with 0.5 mol/L NaNO₃ solution for about 20 to 25 pore volumes at a flow rate of 0.1 mL/min. This flow rate gave an approximate residence time of 6 minutes. At this time, a stop-flow method was applied for 19 hours and then leached for another 10 pore volumes. In a second study, two sediments (SX-108 7A and 41-09-39 7AB) were used. These sediments were leached with 0.5 mol/L KNO₃ solution during the first 25 pore volumes, then followed with 0.25 mol/L $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution for the next 25 pore volumes at a flow rate of 0.1 mL/min. After all the leachates were collected, columns were flushed at 0.1 mL/min with 1.0 mol/L NaNO₃ or KNO₃ and the electrical conductivity monitored to estimate conservative tracer breakthrough. This procedure was followed by flushing the columns with deionized water, then weighing the columns, and determining the pore space as the difference between wet and air-dried sediments.

Sediment leachates were collected every 6 minutes and the mass of solutions determined to better estimate flow rate. After all the leachates were collected, packed columns were flushed with deionized water, weighed, and sediment pore space determined as a difference of wet and

air-dried sediment. The NaNO_3 or KNO_3 leachates were analyzed for Cr(VI) using the diphenylcarbazide colorimetric method (540 nm) (Bartlett and James 1996). In the presence of $(\text{NH}_4)_2\text{C}_2\text{O}_4$, Cr(VI) could not be measured by colorimetry; therefore, liquids containing the oxalate matrix were analyzed for total Cr with ICP-OEC.

D.4.2.3 Results

The sediments used in these studies have variable concentrations of total Cr, Fe, Na, and Cr(VI) and Cr(III); Si and Al content were similar in all four sediments (Table D.4.2.1). The Cr and Na observed in the sediments were the result of tank waste. The Fe, Al, and Si content were a reflection of the sediments' mineralogic assemblage, although Al has been reported to be a major component of the leaked fluids as the $\text{Al}(\text{OH})_4^-$ anion (at concentrations as high as 1.3 mol/L). While XRD and SEM examination of cored sediments did not find evidence of significant Al oxide precipitation, it is likely that Al precipitated soon after entering the soil leaving substantially less Al in solution as it percolated through the sediment column.

Table D.4.2.1. Total Concentration of Selected Elements and Total Concentration of Cr(VI) and Cr(III) in 4 WMA S-SX Sediments.

Sediment	Al	Fe	Si	Na	Cr(VI)	Cr(III)	Cr Total	Cr(VI) %
	%				$\mu\text{g/g}$			
7A	6.45	3.65	29.46	4.37	324	973	1297	25
8A	6.68	3.16	30.49	4.65	1112	986	2098	53
6AB	6.78	3.02	31.38	3.14	605	581	1186	51

The Fe content of these sediments was variable (Table D.4.2.1) and likely a consequence of the natural heterogeneity of the Hanford formation. The source of the Fe (and native Al and Si) is determined by the primary and secondary minerals present in the sediments. Iron oxide content in pristine Hanford sediments is minor; hematite (0.2 wt%) and magnetite (0.4 wt%) are the most abundant Fe oxides. Sediments exposed to simulated tank-leaked wastes (high base, high saline) do show significant decreases in chlorite and smectite, and alteration of micas with slight, concomitant increases in hematite content (Section D. 1.1).

Scanning electron microscopy examination of biotite isolated from pristine sediments and laboratory, base-treated bulk sediments show the potential changes that may occur with sediment exposure to high pH solutions similar to tank-leaked fluids (Figure D.4.2.1). The pristine biotite specimen (Figure D.4.2.1a) exhibits only limited Fe oxide precipitation on its surface, whereas the base-treated biotite surface is covered with secondary precipitates (Figure D.4.2.1 b). The appearance of the reacted biotite is similar to that observed under SEM examination of the SX-108 3A sediment, which was probably the most intensely weathered sediment examined from the slant borehole (Section D. 1.1). With depth away from the tank, observable alterations

of sediment minerals and accumulation of surface precipitates compared to pristine sediments becomes less obvious under SEM examination (Section D.1.1). While mica specimens from 3A show similar impact as those seen in Figure D.4.2.1b, sediment 7A appears only moderately altered, 8A shows only limited surface precipitates, and sediments below this appear pristine. Unfortunately, no comparable examination has yet been performed for the 41-09-39 sediments.

Figure D.4.2.1. Scanning Electron Micrographs of Biotite Grains Showing Fe-Oxides on the Surface, a) From Uncontaminated 200-Area Tank Farm Sediments, and b) From the Same Sediments Reacted with Hyperalkaline (1 M NaOH) Solutions for 24 Days.

Two points relevant to the present Cr discussion need to be made. First, high base fluids contacting Hanford sediment tend to dissolve/alter the smectite and mica fractions. This leads to the precipitation of secondary Fe and Al oxides and zeolites (D.2), but does not change the total Fe content of the sediment. Second, the oxides precipitated on the biotite surface (Figure D.4.2.1b) are suggested to be Ti substituted Fe oxides or perhaps an ilmenite phase (FeTiO_4) (Section D.1.1). The potential for Ti substitution in secondary Fe oxides results from the dissolution of Ti containing smectites and micas. Isomorphic substitution of Ti(IV) for Fe(III) in the Fe oxide structure can impart a permanent positive charge component to the oxide and significantly increase the point of net zero charge of the oxide (Cornell and Schwertmann 1996). This could affect the strength of the chromate-oxide surface interaction at the pH levels observed in these sediments.

The total Cr content and the Cr(VI)/Cr(III) ratio varied in the four sediments studied (Table D.4.2.1). The possible reasons for these variations may be related to: (1) the sediment's position relative to the waste-fluid flow path, (2) the residence time of the fluid, and (3) the nature, rate, and extent of reactions leading to the retardation of the Cr(VI). The first two hypothesized reasons are difficult to access since no spatial distribution information is available other than the two collected cores. The latter aspect of reactivity is being addressed under several EMSP projects and is discussed in several sections of this report (Sections D.4.1, D.4.3, and D.4.4). While there is a small quantity of native Cr present in the Hanford sediments (approximately 60 to 100 $\mu\text{g/g}$ sediment; Serne et al. 2001c) the vast majority of the Cr found under the S and SX tank farms originated from tank leaks. The contaminant ion in the waste supernate was undoubtedly the Cr(VI)O_4^{2-} anion (Lichtner 2001; this report), while the Cr(III)

observed in the sediments (Section D.4.1) resulted from the in situ reduction of Cr(VI). Research by S&T Program and EMSP investigators observe, in laboratory studies, the reduction of Cr(VI) by Fe(II) released from the base dissolution of biotite and by the Fe(II) in magnetite (a mixed valence Fe oxide) (Sections D.4.3 and D.4.4).

Using epoxy-impregnated, 0.1-mm-thick sections of different sediments, Heald (at the APS, Argonne National Laboratory) measured selected regions of SX-108 3A and 7A thin-sections for the distribution of Cr by micro X-ray fluorescence spectroscopy. Figure D.4.2.2 shows the results of such an analysis for sediment 7A as a series of elemental maps for Cr, K, Fe, Mn, and Ti. The bright spots (red/yellow) on the Cr map (Figure D.4.2.2) matched the bright spots associated with K, Fe, Mn, and Ti. These Cr "hot spots" were examined by XAFS spectroscopy and were shown to be Cr(III) (spectra not shown). Five regions in the 7A sediment thin section and two regions in the 3A sediment thin section were interrogated in a similar manner. In every case but one, the Cr species identified was Cr(III). Only one Cr "hot spot" showed the possible presence of both Cr(III) and Cr(VI).

Figure D.4.2.2. A Slice of the SX-108 7A Sediment Thin Section Delineating Region 1 and the Results of the Elemental Micro-Mapping Performed on Region 1; the Colored Bar Shows, Qualitatively, the Concentration of a Given Element (Intensity Increases From Blue to Red).

The "hot spot" in the center of the Cr map (Figure D.4.2.2) was coincident with those of Mn, Fe, and Ti. A SEM of region 1 is shown in Figure D.4.2.3 (bottom micrograph). The bright, circled image was indicative of a titanomagnetite or ilmenite phase (as determined by energy-dispersive spectroscopy). Overlaying the Cr map from region 1 showed that the Cr intensity was associated with titanomagnetite or ilmenite particle, and was Cr(III). This relationship between Cr(III), Fe, Mn, and Ti with a titanomagnetite or ilmenite surface is understandable. Ferrous iron is a common component of titanomagnetite and ilmenite; isomorphous substitution of Mn for Fe^{2+} is also common in these oxide minerals. It is suspected that heterogeneous reduction of Cr(VI) by Fe(II) and Mn(II) occurs at the surface of these oxide minerals with the reduced Cr forming mixed metal (Fe, Mn, and Ti) oxides. It is unclear at this time whether the Fe(II) is dissolved from the titanomagnetite and then reduces Cr(VI), or if Cr(VI) is initially sorbed and subsequently reduced. Similarly, the dissolution of biotite and concomitant solubilization of Fe(II) is thought to affect the reduction of Cr(VI) proximal to the point of Fe(II) release. The two bright spots just below the circle in Figure D.4.2.3 correlate well with a K bright spot in Figure D.4.2.2. The underlying mineral is suspected to be a biotite mica flake. These results complement the findings of Catalano et al. as reported in Section D.4.1. That is, Cr(III) tends to be heterogeneous distributed and isolated to a number of Cr "hot spots," whereas, Cr(VI) is more uniformly distributed throughout the sediment.

Figure D.4.2.3. SEM Image of Region One of a Thin Section of Sediment SX-108 7A with a Biotite Flake Highlighted and the Cr Micro-Map Overlayed.

Chromium was rapidly leached from contaminated S-SX sediments, presumably as the CrO_4^{2-} ion (Figure D.4.2.4, Table D.4.2.2). The initial pulse of Cr(VI) (1 to 4 pore volumes) accounted for 48%, 48%, 67%, and 113% of the Cr(VI) leached from 7A, 8A, 6AB, and 7ABC, respectively. An additional 15%, 8%, 12%, and 14% of the Cr(VI) was leached from 7A, 8A, 6AB, and 7ABC, respectively, after the first 4 pore volumes. While much of the Cr(VI) was leached from the sediments (Table D.4.2.2), 127% of the Cr(VI) was removed from 7ABC. This result reflects variation between subsamples of the same sediment rather than Cr(III) oxidation. It is unlikely that Cr(III) will oxidize under the conditions of these studies (James and Bartlett 1983). The variable release of Cr(VI) from the four sediments studied may result from pH, Fe oxide content, and/or the ionic strength of the solution.

Figure D.4.2.4. Column Effluent Cr(VI) Profiles of WMA S-SX Sediments Leached with 0.5 M/L NaNO_3 .

Table D.4.2.2. Initial and Cumulative Cr(VI) Concentrations From Column Effluents Associated with WMA S-SX Sediments Leached with 0.5 M/L NaNO₃.

Sediment	Cr in sediment			Cr (VI) leached from column experiments			
	Total	Cr (VI)	Cr (III)	Total	Initial ^b	Total	Initial
	μg/g			%			
7A	1297	324	973	206	156	64	48
8A	2098	1112	986	629	537	57	48
6AB	1186	605	581	480	405	78	67
7ABC	2090	1212	878	1542	1374	127	113

^aFirst four pore volumes

^bVersus total Cr (VI) in sediment

Sodium nitrate, probably present as a solid in these sediments, was in substantial excess of the leaching solution. The NaNO₃ (s) was solubilized as the sediment was wetted; hence, the initial NaNO₃ (aq) concentrations were at least (and possibly higher than) 3.6 mol/L, 3.1 mol/L, 2.1 mol/L, and 0.84 mol/L for 7A, 8A, 6AB, and 7ABC, respectively. These values are based on water extracts performed as part of the initial characterization of the sediments (Seme et al. 2001a, b). pH and electrolyte concentration can affect the retention of an oxyanion such as CrO₄²⁻ that forms weak outer-sphere complexes at the surfaces of Al and Fe oxides (Ainsworth et al. 1989; Zachara et al. 1989; Kent et al. 1995) and layer Al silicate edges (e.g., kaolinite; Zachara et al. 1988). At pH values observed in the sediments (9.6 [7A], 8.7 [7ABC], 8.3 [6AB], and 7.8 [8A]), the variable charge surfaces that bind Cr(VI) will manifest neutral to negatively charged surfaces, limiting the formation of outer-sphere complexes involved in sorption. In addition, at the aforementioned ionic strengths, the NO₃⁻ ion could compete with Cr(VI)O₄²⁻ for adsorption sites.

Early, preliminary modeling efforts of the Cr(VI) column data (Figure D.4.2.4) have involved several approaches to identify hypotheses regarding mechanisms controlling the rate of Cr(VI) leaching from the sediments. All initial modeling approaches have assumed one-dimensional saturated transport (i.e., wetting was not included) with one or two reactions to describe CrO₄²⁻ solid-liquid partitioning: (1) no reaction (i.e., tracer breakthrough), (2) fast (i.e., equilibrium) desorption/ dissolution with a single reaction, (3) a single kinetic desorption reaction (first-order), (4) a single kinetic desorption reaction with a limited total mass (i.e., second-order reaction), and (5) two dissolution reactions (each written as pseudo-1st-order). Parameters that are well known (velocity, dispersivity) were fixed during simulations. Hydrodynamic dispersion was determined from tracer data. In these studies, tracer experiments were conducted in each column after CrO₄²⁻ leaching.

Initial modeling results indicated that the initial pulse of soluble CrO_4^{2-} (first 4 pore volumes) could be accounted for by a single first-order kinetic reaction with a small K_d value (less than $0.02 \text{ cm}^3/\text{g}$) and fairly fast rate (approximately 8 to 19 minutes $t_{1/2}$). These parameters are consistent with chromate-salt dissolution (fast), or desorption of a weakly adsorbed species in the face of strong competition. The elution of additional chromate mass in the next 30 pore volumes could not be accounted for by one or two simple pseudo-1st-order reactions, but could be accounted for by a slow fractional order chemical reaction or diffusion process. These latter parameters are consistent with those expected for dissolution of a salt with limited solubility.

The leaching and modeling results indicate that there are multiple species of Cr(VI) in the sediment. The largest fraction (represented by the first 4 pore volumes) is only weakly held against transport. Whether this fraction is a fast-dissolving chromate salt (i.e., Na_2CrO_4) or a weakly bound outer-sphere complex cannot be discerned from these studies. However, there was a second, smaller pool of Cr(VI), defined as the Cr(VI) released beyond 4 pore volumes, which exhibited greater retardation than expected for Cr(VI) in the Hanford sediments. At present, we hypothesize that the second pool of Cr(VI) is represented by CrO_4^{2-} sorbed to secondary Fe oxides. For those sediments most affected by tank-leaked fluids (3A, 7A, and to a lesser extent 8A), the Fe oxides present may exhibit surface properties common to Ti-substituted Fe oxides and present a very different CrO_4^{2-} adsorption potential than typically observed for soil oxides; yielding a larger K_d than expected. Typically, K_d values for CrO_4^{2-} in Hanford aquifers are low; probably below those estimated for the first 4 pore volumes (Jim Szecsody, personal communication).

Batch Cr solubilization studies with $(\text{NH}_4)_2\text{C}_2\text{O}_4$ were performed in conjunction with Cs release studies using sediments SX-108 3A and 7A, and 4109-39 7ABC and 9ABC. Only the results from the 7A and 7ABC studies will be shown here as data is lacking for Cr speciation in the other sediments. Over a period of 32 days, the aqueous concentration of Fe, Al, and Cr (total) increased in a curvilinear fashion (Figure D.4.2.5). While the rate of increase slowed over time, the metal concentrations had not attained aqueous phase steady-state conditions in 32 days. After 32 days, the $(\text{NH}_4)_2\text{C}_2\text{O}_4$ had extracted $1537 \mu\text{g/g}$ Cr from 7ABC [107% of the estimated Cr(VI) or 75% of total Cr] and $778 \mu\text{g/g}$ Cr from 7A [219% of the estimated Cr(VI) or 60% of the total Cr]. It is difficult to rationalize the Cr concentrations observed in the extracts given the XAS results and previously discussed column studies without concluding that the $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solubilized at least some of the Cr(III) in these sediments.

Figure D.4.2.5. Al, Fe, and Cr Solubilization as a Function of Time for Two WMA S-SX Sediments, a) SX-108 7A, and b) 41-09-39 7ABC by 0.25 M/L $(\text{NH}_4)_2\text{C}_2\text{O}_4$.

The solubility of pure amorphous $\text{Cr}(\text{OH})_3$ ($\log K_{sp} = 5.62$) supports about 10^{-3} M $\text{Cr}(\text{III})$ in solution at pH 3 to 4 (Rai et al. 1986). In the present sediments, however, $\text{Cr}(\text{III})$ is suggested to be present as mixed metal oxides (or hydroxides) rather than a pure Cr phase. Amorphous $\text{Fe,Cr}(\text{OH})_3$ solids do form at ambient temperatures and tend to form solid solutions whose $\text{Cr}(\text{III})$ solubility decreases from that observed for $\text{Cr}(\text{OH})_3$ depending on the mole fraction of Cr in the solid (Rai et al. 1986). At low mole fractions expected in geologic environments, Rai et al. reported that the equilibrium aqueous $\text{Cr}(\text{III})$ concentration would be 1 to 3 orders of magnitude lower than that expected from $\text{Cr}(\text{OH})_3$. In the present case, at pH 3 to 4, that would still support substantial $\text{Cr}(\text{III})_{aq}$ concentrations. However, the time required to reach equilibrium $[\text{Cr}(\text{III})]_{aq}$ is a function of its solid solution mole fraction. Rai et al. (1986) found that equilibrium conditions were obtained only after 7 to 90 days depending on the mole fraction of Cr. James and Bartlett (1983) demonstrated that $\text{Cr}(\text{III})$ solubilization and oxidation in soils could be enhanced in the presence of citrate, presumably by complexation; although the rate of $\text{Cr}(\text{III})$ oxidation was dependent on $\text{Cr}(\text{III})$ form. If as suspected from the XAS investigations reported here and by Catalano et al. (Section D.4.1), Cr and Fe are well correlated, then solubilization of Fe oxides by the Tamm's reagent (Loeppert and Inskeep 1996) could facilitate $\text{Cr}(\text{III})$ solubilization. Clearly, there is a potential for $\text{Cr}(\text{III})$ solubilization in 0.25 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ at pH 3 to 4 (by the end of the study the pH had shifted slightly in all sediments to 3.5 to 4.1). At this time, however, the rate of $\text{Cr}(\text{III})$ solubilization and its concentration in these suspensions is not known.

A regression comparison of extract Fe or Al concentrations versus aqueous Cr concentration yield linear relationships with high correlation coefficients (Figure D.4.2.6). The r^2 values for Fe and Al versus Cr extract concentrations are 0.98 and 0.93 and 0.94 and 0.95 for sediment 3A and 7A, respectively. The Al correlation coefficients for these sediments probably reflect the substitution of Al (and other metals) for Fe in all Fe oxides (Connell and Schwertmann 1996) or the presence of poorly crystalline Al oxide phases. An additional source of Al (and Si) may be the slow acid dissolution of layer silicate minerals. While the dissolution rate of layer silicates is slow at pH 3 and 4, the dissolved solids reported in Section D.3.6 (Table D.3.6.2) shows that after 33 days between 1.73 and 2.77% of the sediment mass had been solubilized (based on Fe,

Al, and Si analysis and expressed as oxides). Regardless of the speciation of Cr [Cr(III) and/or Cr(VI)] in these extracts, there is a clear relationship between Cr and sediment Al and Fe oxides.

Figure D.4.2.6. Relationship Between 0.25 M/L $(\text{NH}_4)_2\text{C}_2\text{O}_4$ Solubilized Fe or Al with Cr as a Function of Time for Two WMA S-SX Sediments, a) SX-108 7A, and b) 41-09-39 7ABC.

To further investigate the potential relationship between Fe, Al oxides, and Cr in the sediments associated with the WMA S-SX sediments two additional column experiments were performed. These were similar to the previous column studies except 0.5 mol/L KNO_3 was used to elute Cr(VI) for the first 21 pore volumes, followed by 0.25 mol/L $(\text{NH}_4)_2\text{C}_2\text{O}_4$ for approximately 25 pore volumes. Similar to the NaNO_3 eluted columns, KNO_3 eluted large quantities of Cr(VI) in the first 4 pore volumes (Figure D.4.2.7; Table D.4.2.3). The initial Cr(VI) concentration eluted from sediment 7ABC was about 2 times less than the previous column results ($558 \mu\text{g/g}$ versus $1374 \mu\text{g/g}$), while 7A elution increased slightly ($235 \mu\text{g/g}$ from $156 \mu\text{g/g}$). The variation in these data and in relation to the assumed total Cr and Cr(VI) is related to the variability between samples and is a natural consequence of studying actual sediments. Yet, even with the observed variations, the same precipitous decrease in effluent concentration and cumulative Cr(VI) elution over the initial pore volumes was not significantly changed between the two experiments.

Sediment	Cr in sediment			Cr leached from columns			
	Total	Cr (VI)	Cr (III)	Total	Initial ^a	KNO ₃ ^b	Ox ^c
	μg/g						
7A	1297	324	973	325	235	243	82
7ABC	2090	1212	878	1015	558	644	371

^aInitial = sum of Cr(VI) in first 4 pore volumes.

^bKNO₃ = [Cr(VI)] leached in the first 21 pore volumes by 0.5 mol/L KNO₃ solution.

^cOx = [Cr] leached by (NH₄)₂C₂O₄ beyond 21 pore volumes.

After the initial flush of Cr(VI), its elution from the sediments slowed markedly. After 21 pore volumes, the shift to 0.25 mol/L (NH₄)₂C₂O₄ leaching solution resulted in an immediate increase in Cr elution (see inserts Figure D.4.2.7; Table D.4.2.3). The increase in Cr release from the sediment was substantially greater and long lasting than that observed from a simple stopped-flow as in the previous column studies. While we do not know the speciation of Cr in the oxalate effluents, it was interesting to note that oxalate extracted only a limited amount of Cr and the total Cr leached from the columns did not exceed the expected total sediment Cr(VI) concentration. We are currently attempting to use ion chromatography to determine the Cr speciation.

In addition to the rising Cr concentration, Fe and Al increased concomitantly and the Fe to Cr ratio was stable in both sediments (Figure D.4.2.8). Iron solubilization by the $(\text{NH}_4)_2\text{C}_2\text{O}_4$ for sediment 7ABC was substantially different from 7A in both magnitude and profile. This may be a reflection of the greater Fe content found in 7ABC compared to the other sediments studied (see Table D.4.2.1). It was interesting that the Al solubilization magnitude and profile are similar between the two sediments. This suggests that Al plays a bigger role in the 7A sediment, as discrete, poorly crystalline Al oxide or Al substituted Fe oxides, than 7ABC. Whether this is related to the leaked fluids from tank SX-108, reported to have high $\text{Al}(\text{OH})_4^-$ concentration, it is difficult to surmise. Yet, in both sediments (and in the batch studies) the aqueous Cr concentrations are well correlated to solubilized Fe and Al levels.

Figure D.4.2.8. Profile of Al, Fe, and Cr Concentrations in Column Effluent After Switching Eluents From 0.5 M/L KNO_3 to 0.25 M/L $(\text{NH}_4)_2\text{C}_2\text{O}_4$ at Pore Volume 21 (Only Even Numbered Pore Volumes are Shown for Clarity).

D.4.2.4 Conclusions

These studies, in conjunction with the XAS studies discussed here and by Catalano et al. (Section D.4.1), yields a picture of Cr(VI) dispersed throughout the sediments studied rather than in isolated, highly heterogeneous concentrations as is the case for Cr(III). There appear to be two pools of Cr(VI) in the contaminated sediments studied to date. The largest pool is released rapidly with limited or no retardation. The residual NaNO_3 from tank-leaked fluids appears to assist in the mobilization of this pool of Cr(VI). The second pool of Cr(VI) is more strongly bound to the sediments (albeit only slightly). However, it is unclear at this time whether this division into two pools is an artifact of the high ionic strength of the first few pore volumes or related to (1) the presence of a soluble Cr salt (probably Na based) versus a smaller pool of Cr weakly bound as outer-sphere complexes at oxide surfaces, or (2) different pools of Cr(VI) exhibiting different surface binding strengths. The later time periods of the batch study and particularly the $(\text{NH}_4)_2\text{C}_2\text{O}_4$ leaching clearly showed that the "second pool" of Cr(VI) is associated with the Fe, Al oxide fraction of the sediments. As such, it is subject to competition from the soluble salts found in the sediments. Regardless of the Cr(VI) pool, the majority of the

Cr(VI) currently in the vadose zone is extremely mobile and its retardation, from the results of column studies, appears minimal.

D.4.2.5 References

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D.4.3 FATE AND TRANSPORT OF CR(VI) IN HANFORD SEDIMENTS TREATED WITH AL-RICH, ALKALINE AND SALINE SOLUTIONS

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D.4.3.1 Introduction

Hexavalent chromium should be highly mobile in Hanford vadose zone sediments under alkaline conditions. Amphoteric mineral sorbents will generally be deprotonated, exhibiting negative charge density, and tank waste anions including NO_3^- and OH^- will strongly compete for the few sites with favorable complexation properties. However, recent observations of Cr transport in the S and SX tank farms indicate that the movement of Cr was retarded (Serne et al. 2001d). We have speculated, in our EMSP research, that REDOX waste-sediment reaction has induced conditions favorable to Cr(VI) retardation. Since the hypothesized processes are not well known, the objective of this investigation was to study the mechanisms that control the fate of Cr(VI) in the Hanford sediments treated with Al-rich, alkaline and saline solutions similar to REDOX tank wastes.

D.4.3.2 Experimental Procedure

Saturated one-dimensional miscible displacement experiments to study retardation reactions of Cr(VI) in Hanford sediments were performed under alkaline and high-ionic strength conditions. For this purpose, three columns were packed to similar bulk densities (1.50, 1.47, and 1.53 g/cm³, respectively) with Hanford sediments. A high-performance liquid chromatographic (HPLC) pump was connected to the columns that were oriented vertically inside a water bath at 50 °C. The leaching solutions were injected at the bottom of the columns to eliminate gravity settling. The leaching solutions were prepared in a CO_2 and O_2 free glove box and were kept inside sealed 3 L plastic bottles. The atmosphere above the leaching solution was continuously saturated with helium gas. The column effluent was collected in sealed 60 mL plastic bottles. Approximately 20 mL of degassed deionized-water was added immediately to each sample to dilute the effluent and avoid precipitation upon cooling. Prior to leaching experiments, the soil columns were slowly saturated and leached with degassed deionized-water for approximately 5 pore volumes.

The first column experiment was performed with a pH neutral, 10 mg/L $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$ solution to evaluate the reactive transport of CrO_4^{2-} in the absence of REDOX waste simulants. When the Cr(VI) breakthrough curve (BTC) was completed, indicated by equal input and output Cr(VI) concentrations, the leaching solution was changed to one containing 1M NaOH, 1M NaNO_3 , 0.055 M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 10 mg L⁻¹ Cr(VI) as $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$, hereafter referred to as the alkaline solution. This solution was considered to be a representative of REDOX tank wastes. The second and the third columns were leached from the beginning with the alkaline solution. The fluid residence time in the first, second, and third columns were 8.05, 9.35, and 35.69 hours, respectively.

When chemical steady-state was established in the second column, the flow interruption method (Brusseau et al. 1997) was used to evaluate the Cr(VI) removal rate. Following the termination

of each displacement experiment, the columns were dismantled, and the soil was sliced in 3 cm long sections and washed twice with DI-water. Total amounts of Al, Si, K, Mg, Ca, Ba, Cr, **Mn**, and Fe contents were determined in column effluents and solid sediments using ICP and Energy Dispersive X-ray Fluorescence Spectroscopy (EDXRF), respectively. A UV spectrophotometer was used to measure Cr(VI) in columns effluents. The CXTFIT computer program (Toride et al. 1999) was used to determine transport constants from the soil column Cr(VI) BTC, using the conventional single-region flow concept. The value of the mean pore water velocity ($0.01596 \text{ cm min}^{-1}$) was calculated from experimental data, and was used in the program to determine the values of the two other constants of the convection-dispersion equation, namely dispersion coefficient (D) and retardation coefficient (R).

D.4.3.3 Results

In the absence of REDOX waste simulants, Cr(VI) showed no retardation in the Hanford sediment (Figure D.4.3.1). Although the Cr(VI) BTC exhibited tailing in the upper section where Cr(VI) concentrations were smaller than that in the input solution (10 mg/L), the retardation coefficient calculated with the CXTFIT computer program was less than one ($R = 0.94$). The adsorption of CrO_4 was nonexistent under these conditions. However, when the leaching solution was switched to the alkaline solution, the Cr(VI) concentration in the column effluent decreased steadily and reached the steady-state concentration after approximately 15 pore volumes, which was about 22% less than concentration in the input solution (Figure D.4.3.2). By 100 hours (14 pore volume), 1.75 mg/L chromate was being continuously removed from the aqueous phase. This rate, which continued to the end of the experiment (additional 100 hours), is equivalent to a first-order half-life of 29 hours. It should be noted that the initial Cr(VI) breakthrough was unretarded and removal was gradual, as observed in other columns, suggesting that the removal process was slow or kinetically constrained.

Figure D.4.3.1. Cr Breakthrough Curve in the Hanford Sediments Leached with a Na_2CrO_4 (10 mg/L Cr) Solution.

Figure D.4.3.2. Changes in Cr Concentration in the First Column During Leaching with a Na_2CrO_4 (10 mg/L Cr) Solution, and then with a Solution Containing 1M NaOH, 1M NaNO_3 , 0.055 M $\text{Al}(\text{NO}_3)_3$, and Na_2CrO_4 (10 mg/L Cr) (residence time of 8.05 hours).

Cr(VI) transport was also retarded in the second column, which was leached from the beginning with the alkaline solution (Figure D.4.3.3). A steady-state concentration was reached after approximately 13 pore volumes, and that concentration was 27% smaller than the influent concentration, and 5% smaller than the steady-state concentration observed in the first column. In **this** column, 2.6-mg/L chromate was being continuously removed by 140 hours (15 pore volume), representing a first-order half life of **21.5** hours (slightly faster than that observed in the first column). Again, achieving this chromate removal rate was a gradual process. A strong relationship **was** found between total Cr and Cr(VI) in the column effluents (Figure D.4.3.4). This confirmed that only Cr(VI) was coming out in the column effluents.

Figure D.4.3.4. Cr(VI) versus Total Cr Measured in the Column Effluent.

The time required to establish chromate removal was more clearly shown from the results of the third experiment, in which the fluid residence time (35.69 hours) was higher than that in the first and the second column (8.05 and 9.35 hours, respectively) (Figure D.4.3.5). The decrease in the Cr(VI) concentration in the column effluent was quite significant in this experiment, which was conducted for a greater time period (about 1000 hours). As with the first two columns, initial, nearly unretarded chromate breakthrough was observed (less than 1.2 pore volume) followed by a gradual decrease in the effluent chromate concentration. A steady-state chromate concentration took about 400 hours (11 pore volume) to achieve, during which time step decreases in chromate concentration were observed (i.e., 1 to 11 pore volumes). Pseudo-first order Cr(VI) removal rates were calculated at these step concentrations, and illustrated the gradual increase in the removal rate: (1) half-life of 110 hours by 140 hours or 4 pore volume, (2) half-life of 32 hours by 210 hours or 6 pore volume, (3) half life of 17 hours by 300 hours or 8.5 pore volume, and (4) half-life greater than 9.6 hours by 400 hours or 11 pore volume (Figure D.4.3.5).

Figure D.4.3.5. Changes in Cr(VI) Concentration in the Third Column During Leaching with a Solution Containing 1M NaOH, 1M NaNO₃, 0.055 M Al(NO₃)₃, and 10 mg/L Cr (residence time of 35.69 hours).

The Cr(VI) concentration in the effluent of the third column decreased to zero after approximately 11 pore volumes, and remained at this level for the rest of experiment (Figure D.4.3.5). In fact, by 900 hours (25 pore volume), the chromate removal rate had still a half-life of greater than 8 hours. Approximately 83% of the total amount of Cr(VI) that entered in the column with the leaching solution was retained in the sediments under this column's flow conditions.

The 24 hours flow interruption method applied in the second column (Figure D.4.3.6) indicated nonequilibrium chemical conditions in the system. When nonequilibrium exists, flow interruption may result in a drop in the effluent solute concentration, similar to the one observed in this experiment. The Cr(VI) concentration decreased to nearly zero when flow interruption was applied. Points A and B in the magnified section of Figure D.4.3.6 correspond to the pre- and post-interrupt Cr(VI) effluent concentrations, respectively. The dip in the Cr(VI) BTC showed that under this experiment's flow conditions (fluid residence time of 9.35 hours); the Cr(VI) removal from the aqueous phase was a rate-limited. The Cr(VI) removal continued to proceed during flow-interruption, decreasing, as a result, the Cr(VI) concentration in the aqueous phase. Assuming the 21.5 hours chromate removal rate calculated from the steady state concentration before the stop-flow event, a 24 hours stop flow should have resulted in the removal of an additional 4.6 mg/L chromate, and the Cr(VI) concentration in the effluent after the 24 hour stop-flow event should have not been smaller than 2.8 mg/L. However, the actual chromate concentration observed after the 24 hour stop-flow event was nearly zero, which indicated a somewhat faster chromate removal rate. It is likely, therefore, that other processes augmented the rate of Cr(VI) removal from the aqueous phase. The Cr(VI) breakthrough front reestablished the Cr(VI) steady-state concentration upon recommencing flow (Figure D.4.3.6).

Elevated Cr levels were found in the sediments at the end of experiments, which provides evidence for Cr incorporation in solid phases. The results from the EDXRF analyses conducted in the sediments of the second column at the end of experiment indicated that the Cr content varied from 45 µg/g in the untreated sediment, to 50 and 68 µg/g in the 3-cm-thick layers near the column inlet and outlet, respectively. The fact that the Cr content in the sediments near the column outlet was the largest, indicated, again, that Cr(VI) removal from the aqueous phase was a kinetically controlled process.

As a result of mineral dissolution, the Fe concentration in the effluent of the second column increased to a maximum of about 3.2 mg/L (Figure D.4.3.7). It then decreased toward a steady-state concentration of 0.9 mg/L. In contrast to what was presented above for Cr(VI), the 24-hour flow interruption resulted in an increase in Fe concentration in the aqueous phase, which more than doubled when the stop-flow was applied (magnified section in Figure D.4.3.7). It appeared that dissolution of Fe-bearing minerals continued during the duration of experiment, and that Fe was continuously released into the soil solution. The Fe front reestablished the steady-state concentration (0.9 mg/L) upon recommencing flow (Figure D.4.3.7).

Aluminum concentrations in the effluent of the second column reached a maximum of 1100 mg/L and then decreased to 200 mg/L (Figure D.4.3.8). Since the Al concentration in the input solution was about 1400 mg/L, the significant decrease in Al concentration indicated Al precipitation. This mass loss reaction was more evident when the stop flow was applied (magnified section in Figure D.4.3.7). The Al concentration in the post-interrupt effluents decreased considerably from 600 mg/L to 70 mg/L, and Al breakthrough front reestablished the value of Al concentration after more than 3 pore volumes upon recommencing flow (magnified section in Figure D.4.3.8).

Figure D.4.3.6. Changes in Cr(VI) Concentration in the Second Column During Leaching with a Solution Containing 1M NaOH, 1M NaNO₃, 0.055 M Al(NO₃)₃, and 10 mg/L Cr.

Figure D.4.3.7. Change in Fe Concentration in the Second Column During Leaching with a Solution Containing 1M NaOH, 1M NaNO₃, 0.055 M Al(NO₃)₃, and 10 mg/L Cr.

Figure D.4.3.8. Changes in Al Concentration in the Second Column During Leaching with a Solution Containing 1M NaOH, 1M NaNO₃, 0.055 M Al(NO₃)₃, and 10 mg/L Cr.

D.4.3.4 Conclusions and Implications

The experimental results presented above demonstrated that Cr(VI) transport in the Hanford sediments was not retarded when sediments are treated with neutral solutions, but undergoes retardation after contact with alkaline and saline solutions similar to REDOX tank waste.

The most likely mechanism causing Cr(VI) retardation in the base-reacted sediments was Fe(II) induced reduction to Cr(III) (Rai and Zachara 1986; Early and Rai 1989; Fendorf and Li 1996; Sedlak and Chan 1997; Pettine et al. 1998; Fendorf et al. 2000). The reaction of alkaline and saline fluids with the soil matrix caused dissolution of Fe(II)-bearing soil minerals, like biotite and chlorite, and the release of Fe(II)_(aq). Fe(II) promotes the reduction of Cr(VI), and less soluble, less mobile Cr(III) species may be formed. Because Cr(III) tends to occur in octahedral coordination with oxygen (Peterson et al. 1997), it may also co-precipitate with Fe(III) to form (Fe, Cr) solid solutions, and/or with Al to form hydrotalcite-like soil minerals (Rai and Zachara 1986). Al precipitates were definitely formed during these experiments.

Our results implied that Cr(VI) reduction was a kinetic process controlled by the rate of Fe(II) release upon dissolution, as metered by other competing reactions like ion exchange, adsorption, and precipitation that may act to lower the aqueous phase Fe(II) activity. The observation that Cr(VI) concentrations in the effluents decreased gradually indicated that the Fe(II) mineral dissolution rate and its subsequent reactivity with other aqueous and solid species were important determinants of the Cr(VI) reduction rate. Although we are unaware of reported Cr(VI) reduction rates under alkaline conditions, we suspect it to be rapid because this rate appears to increase at higher pH (Fendorf and Guangchao 1996; Sedlak and Chan 1997; Pettine et al. 1998).

The steady-state Cr(VI) removal rates observed in the different column experiments were likely the balanced effect of mineral dissolution and precipitation reactions involving Fe(II), the reductant, and Fe(III), the oxidized product. However, a mass balance analysis of the Cr and Fe concentrations indicated that most of the Fe(II) that was evolved by base-induced dissolution remained in the column as Fe(II) phases (solid or adsorbed) or oxidized Fe(III) products (Fe(III) oxides). The sediment exhibited a reddish hue at experiment termination indicating Fe(III) oxide formation. A red color was also quite visible in the Hanford sediments after treatment with a 4 M NaOH, 1 M NaNO₃ and 0.88 M Al(NO₃)₃ solution for 7 days in a batch experiment. These results experimentally confirm observations made with Cr⁶⁺ contaminated sediments from the SX-108 slant borehole. Cr migration is partially retarded by Fe(II)_{aq} induced reduction of Cr(VI) to Cr(III). The reaction/reduction extent is dependent on the base (OH⁻) induced dissolution rate of Fe(II) bearing minerals, which is effected by column residence time and OH⁻ concentration. These results suggest that the in situ reduction of Cr(VI) to Cr(III) may no longer be operative in the Cr-contaminated SX-108 sediments.

D.4.3.5 Acknowledgment

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D.4.3.6 References

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D.4.4 CHROMIUM(VI) REDUCTION IN HOMOGENOUS AND HETEROGENEOUS FE(II) SYSTEMS UNDER ALKALINE CONDITIONS AT 50 °C

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D.4.4.1 Introduction

The objective of this EMSP research was to examine the adsorption and reduction of Cr(VI) on specimen biotite, and in homogeneous Fe(II) solutions at high pH, high ionic strength, and 50 °C. These conditions are thought to be representative of field conditions that may have existed during the intrusion of tank SX-108 fluids into the underlying vadose zone.

D.4.4.2 Experimental Procedures

Specimen biotite collected in North Carolina, was obtained from the mineral collection of the OSU School of Natural Resources. The specimen biotite was ground to less than 56 µm with an agate mortar and pestle. This well-studied and characterized biotite sample was used as a precursor to planned studies with weathered biotites isolated from the Hanford and Ringold geologic formations.

The experiments conducted with biotite were prepared as follows. Samples were composed of 40 mL of the model solutions described in Table D.4.4.1 and 0.1 g of the biotite. All samples were prepared in an argon-filled glove box in polyethylene containers and then moved to 50 °C incubator for a reaction time of 1 week.

Sample treatment	Reactant fluid composition
2	1 mol/L NaOH, and 1 mmol/L Na ₂ CrO ₄
3	1 mol/L NaOH, 3 mol/L NaNO ₃ , and 1 mmol/L Na ₂ CrO ₄
4	5 mol/L NaOH, 1 mol/L Al(NO ₃) ₃
6	5 mol/L NaOH, 1 mol/L Al(NO ₃) ₃ and 100 µmol/L Na ₂ CrO ₄
7	5 mol/L NaOH, 1 mol/L Al(NO ₃) ₃ and 10 µmol/L Na ₂ CrO ₄
8	5 mol/L NaOH, 1 mol/L Al(NO ₃) ₃ and 1 µmol/L Na ₂ CrO ₄
9	5 mol/L NaOH, 1 mol/L Al(NO ₃) ₃ and 0.1 µmol/L Na ₂ CrO ₄

The homogeneous reduction of Cr(VI) was examined in the solutions described in Table D.4.4.2. These samples were again prepared in an Ar-filled glove box, in polyethylene tubes and aged for 1 week at 50 °C.

Table D.4.4.2. Reactant Composition in Homogeneous Cr(VI) Reduction Fe(II).

Sample treatment	Reactant fluid composition
1	1 mol/L NaOH
2	1 mol/L NaOH, and 3 mmol/L FeCl ₂
3	1 mol/L NaOH, and 1 mmol/L Na ₂ CrO ₄
4	1 mol/L NaOH, 1 mmol/L FeCl ₂ and 1 mmol/L Na ₂ CrO ₄
5	1 mol/L NaOH, 2 mmol/L FeCl ₂ and 1 mmol/L Na ₂ CrO ₄
6	1 mol/L NaOH, 3 mmol/L FeCl ₂ and 1 mmol/L Na ₂ CrO ₄
7	1 mol/L NaOH, 1 mol/L NaNO ₃ and 3 mmol/L FeCl ₂
9	1 mol/L NaOH, 1 mol/L NaNO ₃ , 3 mmol/L FeCl ₂ , 1 mmol/L Na ₂ CrO ₄ , and 1 mmol/L Na ₂ CO ₃
10	1 mol/L NaOH, 1 mol/L NaNO ₃ , 3 mmol/L FeCl ₂ , 1 mmol/L Na ₂ CrO ₄ , and 10 mmol/L Na ₂ CO ₃

After 1 week the solids from the heterogeneous experiments were separated by centrifugation and the supernates saved for analyses. The solids were washed with deionized water to remove excess salts. A fraction of the washed solids were kept moist in sealed containers and the remainder of the material was freeze-dried. Freeze-dried materials were examined with scanning electron microscopy (SEM) and X-ray Diffraction (XRD). X-ray absorption near edge structure spectra (XANES) were collected on the moist solids at beam line 11-2 of SSRL as described elsewhere in this report.

Solution analyses **was** conducted with a Perkin-Elmer Optical Emission ICP and/or by a Perkin-Elmer graphite furnace AA equipped with Zeeman background correction to quantitate total Cr, Si, Al, Fe and K. W-visible spectroscopy was used to distinguish between dissolved Cr(III) and Cr(VI).

D.4.4.3 Results and Discussion

D.4.4.3.1 Homogeneous Reduction Experiments. Past studies have shown that the reduction of Cr(VI) by Fe(II) involves three, one-electron transfer steps, with the rate of reaction increasing at acidic pH: $\text{Fe(II)} + \text{Cr(VI)} = \text{Fe(III)} + \text{Cr(V)}$; $\text{Fe(II)} + \text{Cr(V)} = \text{Fe(III)} + \text{Cr(IV)}$; $\text{Fe(II)} + \text{Cr(IV)} = \text{Fe(III)} + \text{Cr(III)}$; and the overall reaction can be written as: $\text{Cr(VI)(aq)} + 3\text{Fe(II)(aq)} = \text{Cr(III)(aq)} + 3\text{Fe(III)(aq)}$. The pH of the aqueous system will affect both the amount of Cr(VI) reduced to Cr(III) and the partitioning of Cr(III) between aqueous and adsorbed species.

In our high pH experiments some Cr(VI) was apparently reduced by Fe(II) very quickly and formed red-brown precipitates within seconds after mixing of the initial solutions. However, after 1 week of reaction there was still some Cr left in solution (Table D.4.4.3). UV-vis spectroscopy indicated that this was all in the form of Cr(VI). The quantity of Cr(VI) removal from solution increased with increased initial concentrations of Fe(II). In the absence of Cr(VI) all of the initial Fe(II) remained in solution. However, addition of 1 mmol/L Na_2CrO_4 resulted in complete removal of all detectable Fe from solution. The addition of 1 mol/L NaNO_3 and 0.01 mol/L Na_2CO_3 did not have a significant effect on Cr(VI) reduction.

Table D.4.4.3. Final Solution Composition From Homogeneous Reduction Studies.

Sample treatment	[Cr] $\mu\text{mol/L}$	% ^a change in [Cr]	[Fe] mmol/L
1	n.a. ^b	n.a.	n.a.
2	n.a.	n.a.	b.d. ^c
3	966.2	-3	n.a.
4	786.4	-21	b.d
5	622.9	-38	b.d
6	452.1	-55	b.d
7	n.a.	n.a.	b.d
8	487.0	-51	b.d
9	441.6	-56	b.d
10	442.5	-56	b.d

^a% change from initial composition

^b n o t applicable

^cBelow detection

Buerge and Hug (1999) showed that in homogeneous aqueous solutions of Cr(VI) and Fe(II), the precipitation of finely dispersed, x-ray amorphous colloids with a chemical composition of $\text{Fe}_{0.75}\text{Cr}_{0.25}(\text{OH})_3(\text{s})$ were observed. Chromium(III) hydroxide, including $\text{Cr}(\text{OH})_3(\text{s})$ and the solid solutions $(\text{Cr,Fe}) (\text{OH})_3(\text{s})$, have been observed to precipitate rapidly in moderately acidic to alkaline solutions and expected to be the important solubility-controlling solids for dissolved Cr(III) for a wide range of pH. In the present study, powder XRD measurements of the precipitates in the homogeneous reduction experiments failed to detect any crystalline phases.

D.4.4.3.2 Heterogeneous Experiments. Biotite is a common Fe(II) containing mica in Hanford formation sediments (D.2). Table D.4.4.4 shows the release of K, Si, and Al due to the dissolution of specimen biotite at high pH conditions. In treatments without $\text{Al}(\text{NO}_3)_3$, there was no detectable Al released from the biotite. The concentration of dissolved Si was about 10 times greater in the absence of dissolved Al than $\text{Al}(\text{NO}_3)_3$ -free treatments. There was no detectable Fe in any of the solutions from the heterogeneous experiments.

Table D.4.4.4. Final Solution Composition From the Heterogeneous Reduction Studies.

Sample treatment	[Cr] μmol/L	% ^a change in [Cr]	[Al] mmol/L	% change in [Al]	[Si] μmol/L	[K] mmol/L	pH
1	n.a. ^b	n.a.	b.d	0	2459.3	0.49	13.75
2	0.0	-100	b.d	0	2330.1	0.78	13.56
3	0.0	-100	b.d	0	2376.4	1.36	13.56
4	n.a.	n.a.	265.5	-73	256.7	1.10	13.93
5	765.4	-23	182.9	-82	206.2	0.74	13.78
6	58.1	-94	250.2	-75	284.1	1.00	13.92
7	2.7	-99	266.9	-73	304.8	1.05	13.92
8	b.d. ^c	-100	274.6	-72	256.4	1.34	13.93
9	b.d	-100	259.8	-74	288.8	1.68	13.92

Reduction of Cr(VI) directly by structural Fe(II) in minerals is a possible mechanism of Cr(VI) reduction. Peterson and coworkers (1996) provided evidence for Cr(VI) reduction at magnetite surfaces. It has been shown that Cr(VI) directly reacted with a Fe(II)-containing smectite, formed precipitates on the smectite surface. Ilton and Veblen (1994) demonstrated that Cr(VI) can be sorbed and reduced to Cr(III) at the biotite edge-fluid interface by structural Fe(II).

Eary and Rai (1989) suggested that chromate is not adsorbed to biotite at **high** pH and Zachara and others (1988 and 1989) have shown that chromate is not adsorbed onto iron oxides at pH values greater than 11.5 to 12. However in the present study, reaction with biotite removed from 20 to 100% of the initial Cr from solution (Table D.4.4.4). Figure D.4.4.1 shows Cr, K-edge XANES from treatments 6 and 7 (a and b). The lack of any detectable pre-edge peak clearly indicates the conversion of Cr(VI) to Cr(III). No Cr(VI) reduction was observed in the biotite-free control. During these experiments, we observed that the bottom of the reaction vessels turned red-brown in treatments with initial Cr(VI) concentration less than or equal to 10^{-5} mol/L; this might have been due to the precipitation of an Fe(hydr)oxide as Fe originating from biotite dissolution and was oxidized by Cr(VI). Interestingly, in treatments with greater initial Cr(VI) concentration, there was no visible red-brown precipitates.

Figure D.4.4.1. Cr K-Edge Spectra of Biotite Samples Reacted with Either (a) 1 mmol/L Na_2CrO_4 or (b) 100 $\mu\text{mol/L}$ Na_2CrO_4 , in the Presence of 5 mol/L NaOH, and 1 mol/L $\text{Al}(\text{NO}_3)_3$.

Note: Absence of any Pre-Edge Peak Indicates that all Cr is Present as Cr(III).

It is apparent in the present study that Cr(VI) reduction by biotite did occur at the elevated pH values used. In companion preliminary experiments, we have observed similar patterns of Cr(VI) reduction (in the presence of 1 to 4 mol/L NaOH) in heterogeneous systems containing synthetic magnetite, a magnetic fraction separated from sediments obtained from the Hanford Site and a nonmagnetic, less than 200 μm size fraction of sedimentary material, also obtained from the Hanford Site. Apparently alkaline-induced dissolution of Fe(II) containing solids can indeed result in Cr(VI) reduction.

The capacity of clays to reduce Cr(VI) is correlated with their ferrous iron content (Taylor et al. 2000). Eary and Rai (1989) found that ferrous iron-bearing minerals such as hematite and biotite reduced hexavalent chromium as the minerals underwent dissolution; the rate of reduction was limited by the rate of Fe(II) release from the minerals. They found that the initial rate of chromate reduction is dependent on the dissolution rates of the ferrous iron contents of these minerals. However, the study of Peterson et al. (1997) suggests that reductive sorption of chromate on iron bearing minerals and “zero-valent” iron in the subsurface is a self-limiting process as iron (II) is consumed on the surface, and Cr(III)-oxyhydroxide builds up on the surface. The insulating nature of these layers prevents electron transfer from deep layers, thus bringing redox processes to a halt. The extent to which this occurs in hyperalkaline solutions is not yet known.

Ilton and Veblen (1994) used XPS and SEM to study the reaction of biotites with Cr(VI) solutions they found that Cr is strongly sorbed by the edges of mica books relative to the basal

plane. In fact, much of the chromium associated with the basal plane is sorbed by steps and layer edges. In the present study, SEM images of biotite basal planes and edges did not show Cr-rich precipitates (data not shown).

D.4.4.4 Conclusions and Implications

It is evident from the present study that reduction of Cr(VI) by Fe(II)-containing solids can occur. While not discussed above, the reaction rates appear to increase with increasing NaOH concentration (data not shown). This may be due to base-induced dissolution of the Fe(II)-containing silicates, leading to release of Fe(II) to solution. However, it is not clear why increases in NaOH concentration would accelerate the reduction of Cr(VI) by magnetite (Fe_3O_4) yet our initial experiments suggest that this can indeed occur. The extent to which this happens in field environments (e.g., the Hanford vadose zone) is not clear, but it seems likely that Cr(VI) reduction would occur if sufficient NaOH were available for reaction with Fe(II)-containing solids. Indeed the reduced Cr was identified in field samples from the SX-108 slant borehole discussed elsewhere in this report, and it is worth noting that the most extensive reduction of Cr was found in field samples that had the greatest pH. Thus, the most critical factor in the in situ reduction Cr(VI) to Cr(III) by sedimentary Fe(II) may have been the presence of and persistence of hyper-alkaline solutions in the Hanford vadose zone.

D.4.4.5 Acknowledgment

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D.4.4.6 References

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D.4.5 CONCLUSIONS OF S&T INVESTIGATIONS OF GEOCHEMISTRY AND REACTIVE TRANSPORT BEHAVIOR OF CR

To determine the potential for the in-ground inventory of Cr to migrate as a result of future meteoric recharge or spills from tank sluicing operations, it is important to understand where it is, what are the predominate geochemical species, and what are the reactions that lead to its speciation and distribution. The studies to date by Hanford S&T and U.S. DOE EMSP investigators have developed information, much of which is reported here, that has led to a framework of a conceptual model of Cr reactive transport in the Hanford vadose zone.

From the few WMA S-SX sediments that have been studied, Cr is present as the reduced, cationic Cr(III) and anionic Cr(VI) species. The spatial distribution of the Cr(III) species is heterogeneously dispersed as small "hot spots." These loci of Cr(III) concentrations are often well correlated with the presence of Fe and Mn; and in several instances have been shown to be associated with biotite mica flakes, and titanite-magnetite (or ilmenite). Presumably, the Cr(III) has formed a mixed metal oxide. Chromate, on the other hand, appears to be more uniformly dispersed throughout the sediments. Extraction of Cr concomitant with Fe and Al yields reasonable correlations suggesting that the CrO_4^{2-} anion is associated with Fe and Al oxides; presumably present as weak outer-sphere surface complexes.

Assuming that the Cr loss to the vadose zone from tank leaks was initially Cr(VI), reduction of Cr(VI) occurred as the fluid was transported away from the leak source. The source of electrons for the reduction of Cr(VI) to Cr(III) is suspected to originate from several sources; the reduced Fe(II) present in the mixed valence mineral magnetite, and the reduced Fe(II) and Mn(II) in 2:1 layer-aluminosilicate minerals such as chlorite and biotite mica. All three of these minerals are present in the Hanford formation sediments; with biotite having the greatest abundance. Under the high pH, high salt, and elevated temperature conditions suspected of REDOX leaked wastes, the homogeneous reduction of Cr(VI) by $\text{Fe(II)}_{(\text{aq})}$ is very fast, almost instantaneous. In heterogeneous systems, with biotite or magnetite as the only source of reductant, the rate of Cr reduction is slowed, and follows biotite > magnetite. In column studies with Hanford sediments, residence time has been shown to be an important element in the retardation of Cr(VI) influent; presumably because of reduction. Hence, one must surmise that the rate-controlling step in the reduction of Cr(VI) is the dissolution of Fe(II) and Mn(II) containing minerals. The reduction is followed by the rapid precipitation of mixed metal oxides, essentially at or near the source of reductant release. This hypothesis is supported by the abundance of reduced Cr(III) and its highly heterogeneous distribution as "hot spots" of Cr(III) observed by XAS.

The high pH and elevated temperature of the tank-leaked fluids appears key to the magnitude of the Cr(VI) reduction. Under these conditions, the rate of layer aluminosilicate dissolution is substantially increased, as is the rate Fe(II) reduction of Cr. A question of a sediments reductive power, or potential, is still to be addressed. From X-ray diffraction analysis of sediments impacted by these fluids, it is clear that biotite is still present [as is Cr(VI)]; although there is a substantial decrease in smectite clays and chlorite. The apparent precipitation of REDOX products at or near the source of reductant release suggests that these surfaces may become passivated with time even in the presence of high OH concentrations. Hence, there appears to be a limit to the reduction potential that is well below the concentration of reductant.

Chromate is retained, only slightly if at all, by weak adsorption to secondary Al and Fe oxides at pH and ionic strength conditions of the tank-leaked fluids. Even under neutral pH conditions, the retardation of Cr(VI) was minimal at best (an $R_f < 1$). As fluid flow slowed and eventually stopped the Cr(VI) was held in place. Because of the elevated temperatures, water content decreased, and potentially, Cr(VI) fell out of solution as a soluble Na salt. Either way, one is left with a fairly uniform distribution of Cr(VI) in the sediments.

Hence, one is left with a substantial in-ground inventory of Cr in the S-SX vadose zone sediments. The stability Cr(III) oxides and its limited toxicity minimizes concern for its presence. Cause for concern, however, lies with the inventory of Cr(VI). It is unlikely that the rate of reduction will continue with meteoric recharge as the pH has moderated over time because of the aforementioned dissolution reactions and recarbonization of the high pH fluids by CO_2 . The pH of all sediments is at or below 9.5 and below about sediment SX-108 7A depth (-84 ft bgs) the pH is between 7.2 and 8.3 (typical pH values for the Hanford formation sediments). While mineral dissolution will continue, its rate will be substantially slower and Cr(VI) will have to compete with O_2 oxidation of Fe(II) and Mn(II) released. Other sources of Cr(VI) reduction (e.g., magnetite) will continue but its abundance is limited. Therefore, it must be assumed that the reactions that led to substantial reduction of Cr(VI) will be of limited value in retarding Cr(VI) in the future.

The majority of the Cr(VI) currently in the vadose zone is extremely mobile and its retardation, from the results of column studies, appears minimal. There appears to be two pools of Cr(VI) in the contaminated sediments studied to date. The largest pool is released rapidly with limited or no retardation. The residual NaNO_3 from tank-leaked fluids appears to assist in the mobilization of *this* pool of Cr(VI). The second pool of Cr(VI) is more strongly bound to the sediments (albeit only slightly). However, it is unclear at this time whether *this* division into two pools is an artifact of the high ionic strength of the first few pore volumes or related to (1) the presence of a soluble Cr salt (probably Na based) versus a smaller pool of Cr weakly bound as outer-sphere complexes at oxide surfaces, or (2) different pools of Cr(VI) exhibiting different surface binding strengths.

The implications of the above discussion are clear. There is a large mobile pool of Cr(VI) that will transport with meteoric recharge or because of spills during proposed sluicing operations. Its retardation by uncontaminated sediments below will be minimal and the potential for the Cr(VI) to reach groundwater must be considered reasonable.

D.5.0 MICROBIOLOGY

D.5.1 MICROBIOLOGICAL ANALYSIS OF HANFORD TANK SX-108 VADOSE SEDIMENTS

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D.5.1.1 Introduction

Microorganisms in terrestrial subsurface environments have a major role in the cycling of elements, weathering of rocks and sediments, and on the geochemical properties of groundwater (Fredrickson and Onstott 2001). They also influence the fate and transport of organic and inorganic contaminants. For example, microorganisms are capable of degrading the various organic compounds present in gasoline and petroleum that may leak from underground storage tanks. Scientists and engineers have taken advantage of these processes and have used bioremediation to eliminate organic contaminants, in situ, from soils and sediments. In addition to the degradation of organic compounds, microorganisms can influence the chemistry of inorganic elements via a number of mechanisms including oxidation-reduction reactions, complexation with cell components or biogenic ligands such as siderophores, or general system-level geochemical changes (e.g., pH, pe) as a result of their concerted metabolism. For example, the activity of dissimilatory metal-reducing bacteria can result in the reductive dissolution of Fe and Mn oxides (Lovley 1995) and the reductive precipitation of U (Fredrickson et al. 2000b) and Tc (Wildung et al. 2000). Such reactions can have a profound impact on the fate and transport of these elements.

While the vadose zone is a relatively harsh environment for microbial life, particularly in arid regions, there have been numerous verifications of the presence of viable microbes in the unsaturated zones in both arid and relatively humid climates (see Kieft and Brockman [2001] for a review on this topic). Water potentials in the vadose zone generally do not directly restrict microbial activity *per se*; many microorganisms are relatively tolerant to the matrix water potentials typical of vadose sediments (Kieft et al. 1993). Rather, it is relatively thin, discontinuous water films that retard the transport of solutes and microorganisms. This, in turn, limits microbial access to nutrients and leads to starvation conditions. Our experience with Hanford Site vadose zone sediments is consistent with these general observations.

Viable microorganisms are present at low population densities but in regions where there is evidence of artificial moisture recharge, the size and activity of microbial populations can be significantly higher relative to pristine sediments (Fredrickson et al. 1993; Brockman et al. 1992). Although the physical and chemical properties of the waste that leaked from tank SX-108 would be considered toxic to most life forms, microorganisms have a remarkable capacity for thriving in environments with extremes in pH, temperature, salinity, radiation, and nutrient flux. While certain properties of the waste might be expected to inhibit or even kill indigenous microorganisms, some components could potentially serve as nutrients and possibly stimulate growth and activity. Hence, it is not possible to predict with any degree of certainty the impact

of the tank waste on the microbiology of the vadose sediments beneath tank SX-108 and, in turn, whether microorganisms, if present, could have any impact on contaminant fate and behavior.

The main objectives of this research were to

- obtain preliminary information regarding the microbiological properties of tank SX-108 sediment samples in terms of microbial population size and distribution
- assess relationships between sediment chemical and physical properties to gain insight into possible factors controlling microbial presence and distribution
- characterize microorganisms cultured from tank SX-108 to assess their potential for activities that may influence contaminant fate and behavior
- determine whether nitrate respiring bacteria reduce nitrate to N_2O or N_2 via nitrite or to ammonium; the latter has implications for the fate of radioactive Cs^+ .

D.5.1.2 Experimental Procedures

During late July and early August of 2000, core samples were collected from the vadose zone beneath tank SX-108 of the 200 West SX tank farm on DOE's Hanford Site. **SX-108** cores were sampled at the **337 Building** in accordance with RADCON guidelines and requirements. Due to these requirements, it was not possible to use completely aseptic methods in processing these samples. However, staff with extensive experience in aseptic techniques processed all samples, and we are confident that contamination during sample processing would have been minimal.

Due to complications and costs associated with working with highly contaminated sediments samples, we restricted our initial analyses to methods based on culturing. We recognize the limitations in basing analyses only on culturing in that typically 1% or less of the total population will grow on typical laboratory media. However, a major benefit of culturing is that organisms are available for subsequent analyses to assess whether they have activities that could impact contaminant behavior and fate.

Samples were subjected to a variety of microbiological culturing methods to determine whether microorganisms were present in these samples and, if so, the types of biogeochemical reactions they may potentially catalyze as a result of their metabolism. To this end, a range of microbiological agar and broth media were inoculated with each of 16 sediment samples collected from the SX-108 slant borehole. Targeted microbial functional groups included aerobic heterotrophic bacteria, ammonia- and nitrite-oxidizing autotrophic bacteria, denitrifying bacteria, fermentative bacteria, Fe(III)-reducing bacteria, and sulfate-reducing bacteria. Detailed methods for these analyses have been reported elsewhere (McKinley et al. 1997; Fredrickson and Balkwill 1998). Briefly, both dilution plate counting and broth enrichment approaches were used. Liquid medium was inoculated directly with a standard volume of sediment sampled directly from the cores. For dilution plates, sediment was suspended in the sterile pyrophosphate buffer and mixed vigorously prior to dilution and spread plating on agar medium. Media were incubated at room temperature except where noted as being different.

Agar plates were examined periodically over a period of several months and the number of bacterial colonies determined at several points. Distinct colony types, based on color, size, and morphology, arising on agar plates inoculated with the various samples were noted, picked, and streaked for isolation onto fresh medium. In some instances there was no observed bacterial growth on agar plates as indicated by the lack of bacterial colonies but growth was observed in broth enrichments. In these situations, a small volume of broth enrichment was transferred to fresh medium, including agar plates, in an attempt to isolate additional microorganisms. In this manner, approximately 50 bacterial cultures have been obtained to date from the various core samples. These cultures have been preserved at -80 °C in our laboratories at PNNL and have been deposited in the DOE Subsurface Microbial Culture Collection (SMCC) at Florida State University where they have also been preserved.

A subset of cultures (isolates) was subjected to phylogenetic analysis by sequencing the 16 S rRNA gene. Phylogenetic analysis is a measure of the genetic relatedness of the subsurface isolates to other isolates, many of which have been well described and for which considerable physiological information can be available. Thus, phylogenetic typing can provide insights into the types of metabolic functions associated with the individual cultures. In addition to the phylogenetic analysis, select physiological properties are being conducted on a subset of the cultured organisms. These include resistance to ionizing radiation and desiccation (Mattimore and Battista 1996) and ability to reduce Tc(VII), U(VI), and Cr(VI) (Fredrickson et al. 2000a).

D.5.1.3 Results

D.5.1.3.1 Sediment Microbial Populations. In general, the populations of aerobic heterotrophic bacteria, as determined by dilution plate counts, were quite variable, ranging from below detection to greater than 10^4 colony-forming units (CFU) per gram of sediment (Table D.5.1.1). There were no obvious trends regarding the presence or population size of heterotrophic bacteria in relation depth, radioactivity (^{137}Cs), or volumetric water content. In fact, several sediment samples with relatively low water contents and high radioactivity (54.48, 71.51, and 84.13 m, for example) also contained some of the highest populations of heterotrophic bacteria. Two of the samples, 54.48 and 143.99, contained remarkably high populations for vadose sediments. The factors controlling the presence and size of these populations are currently unclear. Modeling efforts to define the historical thermal regime indicate that sediments beneath tank SX-108 were exposed to temperatures in excess of 100 °C to depths as great as 70 feet beneath the tank for as long as 10 years. This heating and associated desiccation would likely have had a negative impact on the viability of vegetative cells. Additional scrutiny of sediment chemical and physical properties may provide additional insights into the controlling factors. Tank waste constituents, depending on their chemical properties and reactivity with sediments, can migrate at different rates through the sediments. Although some constituents may be toxic to microorganisms, others may have little or no impact while a few, such as nitrogen, carbon, or phosphorous-containing compounds may stimulate the growth and metabolism of endogenous vadose microorganisms. Due to the chemical and radiological characteristics of wastes associated with the Hanford tanks, they would not be expected to support microbial populations. However, because of the ability of microorganisms to survive and even thrive under conditions considered uninhabitable by higher life forms, their presence within the tanks cannot be ruled out (Stevens and Fredrickson 1990). To our knowledge, no microbiological analysis of tank wastes has ever been conducted.

Table D.5.1.1. Populations of Aerobic Heterotrophic Bacteria in Vadose Samples From Beneath SX-108.

Sample ID	Depth feet	¹³⁷ Cs pCi/g	Water content %	PTYG ^a	Viable counts R2A ^b	(log CFU/g) Actino ^c
1a	54.48	3.06E+06	4.3	4.0	4.0	4.0
3a	67.27	1.95E+07	2.8	bd ^d	bd	bd
4a	71.51	1.38E+06	2.8	3.7	bd	2.9
5a	75.73	6.52E+06	4.7	bd	bd	bd
6a	79.94	5.31E+07	3.7	bd	bd	bd
7a	84.13	2.14E+07	6.2	3.2	3.1	3.2
8a	88.32	5.55E+05	6.0	bd	bd	bd
9a	92.48	1.71E+02	2.4	2.6	bd	bd
10a	96.64	4.51E+02	1.9	bd	1.8	bd
11a	101.04	9.12E+02	3.2	bd	bd	bd
12a	104.92	3.37E+02	21.4	2.7	2.7	2.7
13a	113.14	5.21E+02	7.6	bd	bd	bd
14a	121.30	8.37E+02	12.0	bd	bd	bd
15a	129.44	5.92E+02	17.4	bd	1.8	bd
16a	137.54	9.79E+01	7.5	3.3	1.5	bd
17a	143.99	1.75E+02	19.7	>4.3	>4.3	>4.3

^aPTYG = peptone-tryptone-yeast extract glucose medium.

^bR2A = commercially available (Difco Laboratories) medium formulated for culturing aerobic heterotrophic bacteria.

^cActino = Difco medium formulated for culturing actinomycetes.

^dbd = below detection or less than 1.8 log colony forming units (CFU)/g.

Denitrifying bacteria are able to grow with O₂ as a terminal electron acceptor but, in its absence, can utilize NO₃⁻ as an alternative acceptor for energy and growth. As a result of this metabolism, denitrifying bacteria reduce NO₃⁻ to NO₂⁻ and then to N₂O or N₂ or, alternatively, to NH₄⁺ depending upon the microorganism and associated biochemical pathway. Because NO₃⁻ is a common tank waste constituent, we initiated enrichments for denitrifying bacteria. Core samples 12A and 17A are the only samples where the presence of denitrifying bacteria was confirmed. At issue is whether these organisms dissimilate nitrate to N₂O/N₂ or to NH₄⁺. No sulfate-reducing or fermentative bacteria were cultured from any of the samples.

Results from previous microbiological analyses of vadose sediments from the Hanford formation are summarized in Table D.5.1.2 to provide a basis for comparison with the tank SX-108 results. All of the samples reported in this table are either from a borehole located near the Yakima Barricade or from boreholes drilled in the 200 West Area of the Hanford Site. All of these

samples are geologically comparable to the SX-108 vadose samples. The Yakima Barricade is located several miles west of the 200 West Area; this site is pristine in that it has not been impacted by site-related activities. The conclusions from these previous studies indicate that pristine Hanford formation vadose sediments contain few or no culturable aerobic heterotrophic bacteria; 10 of 12 Hanford formation sediments samples did not contain detectable levels of viable aerobic bacteria. One (W15, 31.4m) of the two samples that contained culturable bacteria was impacted by artificial recharge and Contamination associated with wastewater released to the surface in the Hanford 200 West Area (Fredrickson et al. 1993). It was hypothesized that the observed culturable populations were the result of stimulation of dormant endogenous bacteria by recharge waters and, possibly, associated nutrients. Additional support for this hypothesis was provided by Kieft et al. (1993) who observed bacterial cells, by direct microscopy, in the range of 10^6 to 10^7 cells/g in pristine Hanford formation sediments. Also, studies by our laboratory (Fredrickson et al. 1995; Brockman et al. 1998) and others (Haldeman et al. 1994) have indicated that populations of viable aerobic heterotrophic bacteria in vadose sediments increase with increasing post-sampling time, sometimes by as much as 6 orders of magnitude, within a period of 10 to 80 days. Post-sampling increases in viable microbial populations in vadose sediments are likely due to stimulation of dormant cells via a variety of possible mechanisms. These mechanisms may include the redistribution of cells and solid-phase associated nutrients by sample mixing or disturbance during coring, by increasing gaseous exchange or by facilitating movement of moisture via evaporation or condensation to generate microscale chemical gradients at surfaces. It should be noted that the time elapsed between coring and inoculation of medium with SX-108 vadose core samples was approximately 30 days.

Table D51.2. Microbiological Properties of Hanford Formation Vadose Sediments From Previous Sampling Efforts.

Borehole	Depth (meters)	Viable counts (log CFU/g)	% H ₂ O	Reference
Yakima Barricade	Surface	6.9	1.6	(Fredrickson et al. 1993)
Yakima Barricade	30.3	2.3	3.9	(Kieft et al. 1993)
Yakima Barricade	31.1	bd ^a	2.2	(Kieft et al. 1993)
Yakima Barricade	31.6	Bd	4.2	(Kieft et al. 1993)
Yakima Barricade	31.8	Bd	7.7	(Fredrickson et al. 1993)
Yakima Barricade	45.8	Bd	2.5	(Kieft et al. 1993)
Yakima Barricade	47.0	Bd	16.1	(Fredrickson et al. 1993)
Yakima Barricade	53.0a	Bd	3.4	(Fredrickson et al. 1993)
Yakima Barricade	53.0b	Bd	1.7	(Kieft et al. 1993)
W18	24.4	Bd	4.5	(Fredrickson et al. 1993)
W18	24.6	Bd	2.9	(Kieft et al. 1993)
W15	31.3'	Bd	11.7	(Kieft et al. 1993)
W15	31.4'	3.1	7.0	(Kieft et al. 1993)

^abd = below detection or less than 2.0 log colony forming units (CFU)/g.

^bsediments subjected to artificial recharge, contamination by past site activities (Fredrickson et al. 1993).

D.5.1.3.2 Isolate Phylogeny: Approximately 50 cultures of aerobic heterotrophic bacteria have been isolated and purified from the various enrichments and dilution plates. These isolates have been preserved by freezing in glycerol at -80 °C and have been shipped to the SMCC at Florida State University for archiving and phylogenetic analysis based on 16S rRNA gene sequence. The phylogeny of the isolates is, for the most part, unremarkable. The genera represented are typical soil and sediment inhabitants. Interestingly, members of the genus *Arthrobacter* were the most common isolates with 5 of 15 isolates being assigned to this genus (Table D.5.1.3). Members of the genus *Arthrobacter* were also found to represent approximately one-third of the aerobic chemoheterotrophic bacteria isolated from pristine Ringold Formation sediments obtained from the Hanford Site Yakima Barricade borehole (Balkwill et al. 1997), drilled as part of DOE's Subsurface Science Program. These strains of *Arthrobacter* appear to represent novel species within the genus (Crocker et al. 2000). Additional genera found as part of this research that were also found in the previous study by Balkwill et al. include *Rhodococcus*, *Staphylococcus*, *Nocaroides*, *Blastobacter*, *Nocardioides*, and *Sphingomonas*. Hence, it appears that the organisms isolated as part of this study are largely common inhabitants of suprabasalt subsurface sediments on the Hanford Site. The isolates characterized to date, except for *Pseudomonas*, *Sphingomonas*, and *Blastobacter*, are predominantly Gram-positive bacteria. Gram-positive bacteria appear to be dominant in many vadose zone environments (Kieft and Brockman 2001), possibly because they are better adapted for survival under low moisture and nutrient starvation conditions. Although some strains of *Sfaphylococcus* are known to be human pathogens, the isolate identified as a member of this genus, 4b-2, is most closely related to a strain obtained from an environmental sample of unknown origin and is not known to be a human pathogen. In addition, *Sfaphylococcus* members represented 20 of 169 isolates cultured from the Yakima Barricade Ringold sediment samples (Balkwill et al. 1997) and thus appears to be a normal component of the vadose zone microbiota on the Site.

Perhaps the most intriguing finding of this research is the isolation of a strain, 7b-1, that is closely related to *Deinococcus radiodurans* (Table D.5.1.3). *Deinococcus radiodurans* is the most radiation-resistant organism discovered to date, exhibiting the ability to withstand doses of ionizing radiation to 15,000 Gy without lethality (Daly et al. 1994). Interestingly, the sediment sample that this bacterium was isolated from had one of the highest levels of radiation (Table D.5.1.1) of any of the samples examined. This is the first isolation, that we are aware of, of a strain of *D. radiodurans* from a radionuclide-contaminated environment. In addition to 7b-1, there are several additional strains isolated from highly contaminated samples that also appear to be members of *Deinococcus*, based on their distinct morphology (Figure D.5.1.1). These strains have recently been submitted to the SMCC and are being sequenced (16S) for phylogenetic analysis.

Table D.5.1.3. Phylogeny of Select Aerobic Heterotrophic Isolates From SX-108 Sediment Samples Base on 16S rRNA Gene Sequence Analysis.

Isolate ID ^a	Phylogeny	GenBank Accession Number
1b-1	<i>Arthrobacter globiformus</i>	M23411
1c-1	<i>Arthrobacter oxydans</i>	AJ243423
4a-4	<i>Rhodococcus corynebacteroides</i>	X80615
4b-2	<i>Staphylococcus warneri</i>	AJ223451
4b-3	<i>Nocardioides plantarum</i>	Z78211
7b-1	<i>Deinococcus radiodurans</i>	Y11332
9c-3	<i>Blastobacter</i> sp. str. BF10	AJ223453
10c-2	<i>Sphingomonas</i> sp. str. Koll-1	AJ224938
12a-1	<i>Pseudomonas</i> sp. str. BRW3	AF025351
12b-1	<i>Pseudomonas</i> sp. str. BRW3	AF025351
15a-1	<i>Terrabacter tumescens</i>	X83812
17a-1	<i>Arthrobacter aurescens</i>	X83405
17a-2	<i>Arthrobacter oxydans</i>	AJ243423
17a-3	<i>Pseudomonas</i> sp. str. BRW3	AF025351
17b-1	<i>Arthrobacter pascens</i>	X80740

^aThe first two digits of the isolated ID refer to the sample from which the culture was isolated.

Figure D.5.1.1. Scanning Electron Microscopic (left) and Transmission Electron Microscopic Image of *D. radiodurans* 7b-1 Cells.

D.5.1.3.3 Characterization of *Deinococcus radiodurans* 7b-1. *D. radiodurans*, at this dose of radiation, incurs a large number of double-stranded DNA breaks, 130 per chromosome (Daly et al. 1994). Extremely efficient DNA repair mechanisms in operation during recovery in the absence of radiation are responsible for the extreme radiation resistance observed in this organism (Daly and Minton 1995, 1996; Minton 1996). We evaluated the resistance of strains 7b-1 and 7c-1 along with *Deinococcus radiodurans* R1, the type strain, to acute doses of ionizing radiation from a ^{60}Co source. The results from this experiment indicate that strains 7b-1 and 7c-1 (not shown) are equally or slightly more resistant to ionizing radiation than *D. radiodurans* R1, the type strain (Figure D.5.1.2). At a dose of 1 MRad, there was no apparent impact on cell growth of either R1, 7b-1, or 7c-1. At a dose of 2 MRad, approximately 0.2% of the cells survived and grew whereas at 3 MRad there was no detectable survival or growth. Resistance to such high levels of ionizing radiation may not represent a direct adaptation response since there are no natural terrestrial environments that generate such high fluxes of ionizing radiation (Minton 1996). It is more likely that the efficient DNA repair system in this bacterium represents an adaptation to prolonged desiccation as dehydration of cells results in DNA damage (double-stranded DNA breaks) similar to that resulting from exposure to ionizing radiation (Mattimore and Battista 1996). It is possible that *Deinococcus* is an indigenous inhabitant of Hanford soils and that the combination of contamination, heating, and drying of sediments led to conditions that only highly stress-tolerant organisms such as *Deinococcus* could survive.

Recently, we demonstrated that *D. radiodurans* R1 was capable of reducing Fe(III) when complexed with nitrilotriacetic acid (NTA), Cr(VI), U(VI), and Tc(VII) and anaerobic conditions with lactate or pyruvate as an electron donor (Fredrickson et al. 2000). Prior to this, *D. radiodurans* was believed to have a strictly aerobic metabolism. These previous findings coupled with the metal and radionuclide contaminants associated with the SX-108 vadose samples (Cr, Tc, U, among others) prompted investigation into the potential for the SX-108 isolates to reduce metals and radionuclides. Our results demonstrate that, similar to *D. radiodurans* R1, 7b-1 also reduced Tc and U under anaerobic conditions but only in the presence of anthraquinone-2,6-disulfonate (AQDS) (Figure D.5.1.3a, b), an organic compound that can function as an electron acceptor and shuttle electrons between cells and metals external to the cell surface. In contrast, 7b-1 was able to reduce Cr(VI) under both aerobic and anaerobic conditions and in the absence of AQDS. The reason for the requirement for AQDS for the reduction of Tc and U but not Cr by *D. radiodurans* are unclear but we previously speculated that it may be due to the inaccessibility of Tc and U to electron transfer enzymes associated with the cells (Fredrickson et al. 2000). In contrast, Cr and AQDS would have access to enzymes that the Tc and U do not. Also similar to *D. radiodurans* R1, 7b-1 was able to reduce Fe(III)-NTA coupled to pyruvate oxidation (Figure D.5.1.4a) and could reduce ferrihydrite only in the presence of pyruvate with AQDS as an electron shuttle (Figure D.5.1.4b).

Figure D.5.1.2. Resistance to Acute Doses of Ionizing Radiation as Measured by the Percentage of Cells Surviving and Growing on Tryptone-Yeast Extract-Glucose Agar Medium Following Exposure to Acute Doses of Gamma Radiation From a ^{60}Co -Source.

Figure D.5.1.3. Reduction of U(VI) (a), Tc(VII) (b), and Cr(VI) (c) by *D. rudiolurans* 7b-1 in TYG for U and Tc and in a pH 7 Bicarbonate-Buffered Medium for the Cr Experiment. AQDS, when Present, was Added a Concentration of 100 μ M.

Figure D.5.1.4. Reduction of Fe(III)-NTA in Bicarbonate-Buffered Medium (a) and Ferrihydrite (b) by *D. rudiolurans* 7b-1.

D.5.1.4 Conclusions and Implications

Although the factors influencing the microbiological characteristics of the SX-108 vadose sediments are unclear at this time, the finding of significant populations of aerobic heterotrophic bacteria may have important implications for the fate and transport of waste-associated contaminants. Microorganisms, in general, have the capacity for a wide range of biogeochemical transformations including reactions with waste constituents. For example, microorganisms are capable of degrading a wide range of organic compounds, oxidizing and reducing multivalent metals and radionuclides such as U or Tc, oxidizing ammonium to nitrite and nitrate and reducing nitrate or nitrite to ammonium or N_2 and for sorption and/or assimilation of a range of cations, including Cs and Sr. An important consideration is whether the denitrifying bacteria that were cultured can dissimilate nitrate or nitrite, in the absence of O_2 , to ammonium or gaseous end products such as N_2O or N_2 . Ammonium effectively competes with Cs for cation exchange sites on soil and sediment particles and has been used to effectively extract exchangeable Cs from soils. The implications would be that the potential exists for the in situ microbiological production of NH_4^+ that could compete with Cs^+ for exchange sites on sediment particles.

As a result of this research, we have confirmed the presence of microorganisms in highly contaminated sediments beneath tank SX-108 and that some of these organisms can utilize nitrate as an electron acceptor in the absence of O_2 while others can reduce several of the contaminating metals and radionuclides to poorly soluble species. The culturable microbiota is composed predominantly of aerobic chemoheterotrophic bacteria, mainly Gram-positive bacteria. These bacteria are generally well adapted to survival under low moisture and low nutrient conditions.

The most remarkable result was the isolation of several ionizing radiation-resistant bacteria closely related to *Deinococcus rudiolurans* from one of the most highly contaminated core samples that was collected. This is the first time that *D. rudiolurans* has been isolated from a radionuclide-contaminated environment to our knowledge. These organisms were able to reduce U(VII) and Tc(VIII) to poorly soluble species in the presence of an electron-shuttling quinone under anoxic conditions. In contrast, these strains were able to reduce Cr(VI) under anaerobic and aerobic conditions with a suitable electron donor. It is unlikely, in our opinion, that metal reduction has or would be occurring in situ for several reasons including the fact cell populations were relatively low, a few tens or hundreds of cells per gram and that the low moisture content would restrict metabolic activity by limiting nutrient flux. However, the possibility of microsites with higher bacterial populations and levels of metabolic activity cannot be ruled out. The presence of such sites could contribute to the reduction of contaminants such as Cr(VI) or NO_3^- , that are easily reduced relative to U and Tc. Reduction of Cr(VI) to relatively insoluble Cr(III) would limit the mobility of this important contaminant in the subsurface.

Additional investigations are required to determine the phylogeny of the remaining isolates and the metabolic capabilities of these organisms that may influence contaminant fate and transport in the vadose zone. Microbial processes may have an even greater impact on contaminant fate and transport in the subsurface under other leaking tanks at Hanford, such as at the B and BX tank farms, where the concentration of organic complexing agents associated with the tanks wastes was much higher than at SX tank farm. Many of the organics associated with the waste, such as citric and tartaric acids, are readily metabolized by a wide range of microorganisms.

The microbial degradation of these organic complexing agents could have a major impact on the migration of contaminants in the vadose zone.

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D.6.0 TRANSPORT MECHANISMS INFERRED BY ISOTOPE GEOCHEMISTRY

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Mass spectrometric methods for determination of stable and long-lived radiological isotope concentrations and concentration ratios have long been used for a wide range of geotechnical investigations including such diverse applications as age dating, paleotemperature measurement, tracking of groundwater and seawater movement, mineral exploration, and chemical source attribution. In spite of such widespread use within the research community, stable isotope methods tend to be very specialized and have found limited use for routine application on environmental investigations. For the past 4 years, researchers at the Lawrence Berkeley National Laboratory (LBNL) Center for Isotope Geochemistry and Pacific Northwest National Laboratory (PNNL) have been experimenting with a suite of mass spectrometric methods aimed at applying powerful stable and long-lived radiological isotope analysis techniques to obtain a better understanding of sources and sinks for water and contaminant movement in the vadose zone and groundwater at DOE sites. In the past 2 years the principal focus of that work has been the Hanford Site. Most recently, under Hanford S&T Program support, uncontaminated and tank leak contaminated core samples from the SX tank farm environs have been subjected to detailed analysis for the isotopes of H, O, Sr, Cs, Mo, I, Se, and U using several different mass spectrometric procedures. Results of those studies are discussed below for three specific topic areas: (1) fission product isotopic fingerprints of waste movement measured in SX tank farm boreholes, (2) horizontal transport of chemical waste inferred from isotopic and chemical measurements of core samples from B8812 clean borehole, and (3) vertical distribution $^{86}\text{Sr}/^{87}\text{Sr}$ isotopic ratios measured in B8812 core and implications to water infiltration near the SX tank farm. The first topic discusses work performed at several PNNL labs. The second represents a collaborative effort between LBNL and PNNL, while the Sr isotope work was performed entirely at LBNL.

D.6.1 FISSION PRODUCT ISOTOPIC FINGERPRINTS OF WASTE MOVEMENT MEASURED IN SX TANK FARM BOREHOLES; IMPLICATIONS TO MOBILE CONTAMINANTS

D.6.1.1 Introduction

While waste tank leaks at Hanford have been recognized since at least the late 1950s, a relatively limited amount of research has been directed toward obtaining a detailed understanding of the geochemical behavior of the diverse collection of contaminants released by tank leaks. In the past few years, a greatly increased level of effort has been undertaken to improve our overall understanding of contaminant movement in the vadose zone and, in particular, the potential for groundwater impact from the more mobile constituents. The recent recognition of groundwater impacts at several tank farms (Johnson and Chou 1998; Narbutovskih 1998; Hodges 1998; Hodges and Chou 2000) has added a degree of urgency to this effort. Recent drilling efforts in the vicinity of the SX tank farm have yielded good quality research materials from cores collected at locations associated with leaks believed to be originating from tanks SX-115, SX-109, and SX-108. All three boreholes were found to be contaminated with tank leak material to some degree. The SX-108 borehole was drilled on a 30-degree slant providing material from the heart of the contaminant plume itself for the first time at Hanford. The SX-108 slant borehole thus represents an ideal source of research materials and has consequently become the central theme of a wide range of focused and detailed research efforts supported by DOE/EMSP and augmented by the Hanford S&T Program. All three cores have been managed and intensively studied by a project supported by the Office of River Protection and implemented at PNNL. Results of those studies are discussed in detail elsewhere in this report and in dedicated individual topical reports for each borehole (Serne et al. 2001a, b, c). Materials and data generated by that effort were used in planning and implementing the work described below.

In order to correctly interpret contaminant distributions in these cores with regard to geological and geochemical controls, it is first necessary to understand the temporal and spatial history of the leaks. For example, essentially all contaminants observed in the SX-108 core show two or more concentration maxima. The multiple peaks can be interpreted as resulting from geologic effects (stratification, grain size), geochemical effects (sorption, precipitation, REDOX), or differences in chemical speciation (valence states, ligand complexation). Alternatively, multiple leak events representing different points in time and volumes of liquid may be responsible for affecting the vertical distribution of contaminants. The effect of multiple events will inevitably be superimposed on top of other effects of more fundamental interest and must be unfolded. Separate leak events originating either from different tanks or separate fillings of the same tank should be resolvable through differences in materials containing internal isotopic signatures. Suitable systems, which have been identified in this work, include the fission-derived isotopes of Cs, Mo, Se, and I. The ^{137}I to ^{129}I ratio of waste is particularly diagnostic. Isotopes of Pu and U also form ideal tank signatures, possessing in principle at least, distinctive fingerprints. Neither element has been observed in significant quantity associated with tank leaks in the SX tank farm, however, because of essentially 100% association of those species with the solid phase in those tanks with correspondingly negligible concentrations found in the leaked supernate. Both Pu and U have been observed in tank leaks from other farms (e.g., tank T-106) and are thus expected to be of great value in future investigations. Alternatively, the ratios of various chemical species with little or no retardation following release from a tank into the vadose zone can also be useful

as indicators of different source compositions. Species, which are used for that purpose here, include Cl, N, S, and ^{99}Tc . More detailed discussion on the considerations affecting each will be discussed separately below.

An additional goal of this work is the identification and baseline characterization of isotopic fingerprints, which may be used for source attribution of groundwater plumes. Association of groundwater contaminants with specific waste management units is typically very difficult at Hanford because of the close spacing of tank farms, cribs, trenches, ponds, operational spills, and other methods for waste to enter the subsurface. Isotopic fingerprinting techniques can provide a means to distinguish between crib waste and tank waste by providing a better definition of the isotopic composition of distinct waste sources than can be inferred from direct measurement. The SX tank farm coring program provides the first real opportunity to obtain some of that information in a suitable form.

Extensive experimentation is currently underway to better understand the mobility of ^{137}Cs in the subsurface. Sorption effects on the surfaces of clay minerals dominate transport of Cs. Since sorption of ^{137}Cs must compete with other chemical forms of Cs including stable ^{133}Cs and the very long-lived ^{135}Cs ($T_{1/2} = 2.3$ million years), both of which are themselves high-yield fission products, it is important to know the total Cs content of the system in order to properly conduct and interpret Cs sorption studies and utilize that data in transport models. Cs isotopic studies reported here combined with nuclear modeling calculations performed in association with that work address the issue of competitive Cs sorption.

D.6.1.2 Experimental Procedures

D.6.1.2.1 ICPMS Analysis. All analyses were performed on either 1:1 water or strong nitric acid extracts of the sediment samples. Extraction was performed by PNNL/ORP staff in the 3720 Building prior to performance of comprehensive analysis on those extracts. Analyses routinely performed on the water and acid extracts included trace metals by ICP-OES and ICP/MS, common anions by ion chromatography, as well as radiological measurement for ^{137}Cs , tritium, ^{90}Sr , ^{99}Tc , and actinides. Details on the experimental protocols used and the results obtained are reported elsewhere in a series of topical reports (Serne et al. 2001a, b, c) and summarized in the main body of this report. Following completion of that work, the remaining extracts and associated blanks, each typically only a few milliliters, were transferred to the 329 Building for more detailed mass spectrometry. Since the samples were highly radioactive, transfer of the samples required appropriate shipping and monitoring protocols for radioactive transfers and all work in the 329 Building was performed under the protocols specified in a Radiation Work Procedure (RWP) specific to that job. A "hot" ICP/MS instrument was dedicated to this activity. Since the "hot" machine was an older instrument with reduced sensitivity (VG PlasmaQuad), some modification of the instrument ion source and vacuum system were required prior to running the samples in order to obtain the requisite instrument sensitivity. Prior to detailed analysis, all samples were screened in the mass range from 91 to 139 and 200 to 243 amu to evaluate potential mass interferences and required dilution factors. Following the screening and determination of appropriate dilution factors, chemical separations were performed on aliquots of the leachates to remove interfering species. ICP/MS analysis was then performed using time resolved ion chromatography/ICP/MS.

D.6.1.2.2 Nuclear Modeling. As an aid to better understanding isotopic ratio measurements, a simple nuclear model was developed to calculate expected ratios of fission-produced Cs, Tc, and Mo. The method employed is very similar to that used in an earlier PNNL study performed for the Nuclear Regulatory Commission (NRC). Details of the FORTRAN-based computer code developed for the NRC work are described in two publications (Evans 1983). A streamlined version of the calculational method used for the NRC study was adapted to a simple Excel spreadsheet. Input data included neutron flux and thermalization parameters for a production reactor, fission and neutron capture cross sections and resonance integrals, fission yields from ^{235}U and ^{239}Pu , and ^{235}U composition for typical production reactor fuel (0.71% ^{235}U).

The spreadsheet performed a series of neutron capture and fission event calculations on 0.1-day intervals for up to 150 days to simulate a typical production reactor irradiation during the REDOX Process era at Hanford. Minor adjustments were made to reactor parameters in order to match expected $^{239}\text{Pu}/^{240}\text{Pu}$ composition at the end of the irradiation period as well calculating reasonable values for ^{235}U burnup and ^{239}Pu accumulation. An average plutonium composition taken from the Best Basis Inventory documents on tanks SX-108 and SX-109 was used to estimate the expected plutonium composition at the end of irradiation (4.5% ^{240}Pu). ORIGEN2 calculations performed by Watrous and Wootan (1997) were also reconciled as a cross-check for accuracy.

Calculated fission product ratios for Mo and Tc proved to be relatively insensitive to reactor parameters and should thus be reasonably reliable indicators of expected ratios to be compared with the measured values. Table D.6.1.1 lists the expected Cs, Tc, and Mo composition on a relative basis in the reactor fuel at the end of a 110-day irradiation producing plutonium containing 4.5% ^{240}Pu . All results are normalized to ^{99}Tc and assume no chemical fractionation effects. Relative ^{137}Cs values shown in Table D.6.1.1 were corrected for decay assuming a 40-year age for the waste based on the tank leak history for tank SX-108 (WHC 1992). The greatly reduced amount of ^{135}Cs shown in Table D.6.1.1 relative to other similar high-yield fission products is the result of burnup of its parent on the beta decay chain, ^{135}Xe . ^{135}Xe has an exceptionally high neutron capture cross-section, 2.65 million barns. The half-life of ^{135}Xe , 9.1 hours, is long enough that in a high flux reactor burnup is actually favored over decay. Because of this situation, the amount of ^{135}Cs produced is extremely sensitive to reactor flux conditions. The measured values of ^{135}Cs and ^{137}Cs can thus be used to tightly constrain input parameters for the model. The extreme sensitivity of the Cs isotope ratios to reactor conditions also suggests that some source related variability can be expected.

Isotope	Relative concentration
^{99}Tc	1.000
^{95}Mo	0.994
^{97}Mo	0.938
^{98}Mo	0.923
^{100}Mo	1.014
^{133}Cs	1.078
	0.33
$^{137}\text{Cs}^*$	0.40

D.6.1.3 Results

D.6.1.3.1 Cesium Isotopes. The ^{137}Cs distribution in the SX-108 slant borehole is shown in Figure D.6.1.1. The plot is based on gamma counting data as reported by Serne et al. (2001c). As a point of comparison, the ^{99}Tc concentrations measured in this study on water leach samples from the same core are plotted on the second axis. Both distributions clearly show two peaks with the unretarded ^{99}Tc penetrating much deeper and with more vertical dispersion evident.

Figure D.6.1.1. Vertical Distributions of ^{137}Cs and ^{99}Tc in SX-108 Slant Borehole.

Cs isotopes were measured by ICP/MS on selected water and acid leach samples near the two peaks in the ^{137}Cs vertical distribution. The results of those measurements are shown in Table D.6.1.2. Only data with relative errors of order 10% or less as determined by replicate

analysis are included in the table. It is clear that, as expected, the acid extracts resulted in the dissolution of a large amount of native Cs from the mineral matrix of the host sediment. ^{133}Cs results from the acid extracts are thus of little value; however, the ratio of ^{137}Cs to ^{135}Cs is of interest because the ratio can be determined in the acid extracts with very good precision and is unaffected by interferences. The ratio appears to be relatively constant across both peaks. The water leach data does show a small difference between the two peaks but it is unclear if that is significant as it may be an artifact of the larger measurement error on the water leach samples. The Cs data is inconclusive with respect to the issue of separate sources for the two peaks. Additional data from different sources is needed to fully understand the dynamics of this isotopic system.

Additional Cs isotopic measurements were also performed on three samples associated with a series of leaching experiments described in more detail elsewhere in this report. Two of the samples were from the two respective Cs maxima in the SX-108 slant borehole while the third was from the ^{137}Cs maximum in the borehole associated with the SX-109 tank leak (41-09-39). The sediment samples were contacted with a very concentrated electrolyte (5 M NaNO_3) for 31 days prior to sampling for Cs isotopics. The measured total Cs to ^{137}Cs ratio in these samples is on average essentially identical to that seen in the water leaches from *tank* SX-108. These data (Table D.6.1.3) show no significant difference at all between the two SX-108 *tank* peaks and only a very small (about 5%) difference for the SX-109 tank event. It appears that based on this very limited information, REDOX waste does not exhibit a very large range of variation in the rate of ^{135}Cs production in spite of the high dependence on reactor conditions found in the nuclear modeling work. The measured concentration ratio of total Cs to ^{137}Cs shown in the table (4.75 ± 0.18) may be used with a high degree of confidence for interpreting Cs sorption experiments with respect to competitive chemical sorption of Cs.

Table D.6.1.2. Cesium Isotopic Measurements in Water and Acid Leaches.

Sample	Vertical Depth Feet BGS	Total Cs-137 pCi/gm	Cs-133 Abundance	RSD %	Cs-135 Abundance	RSD %	Cs-137 Abundance	RSD %	Cs-137/Cs-135	Total Cesium/Cesium137
Acid Extracts										
S0070-01-AE	55.4	3.06E+06	0.932	0.1	0.0287	0.8	0.0392	2.3	1.37	25
S0070-01-AE-Dup	55.4	3.06E+06	0.939	0.03	0.0251	0.3	0.0357	1.1	1.43	28
S0070-03-AE	68.4	1.95E+07	0.741	N	0.108	0.3	0.152	0.9	1.41	6.6
S0070-04-AE	72.7	1.38E+06	0.984	0.1	0.0063	2.8	0.0093	8.0	1.48	108
S0070-05-AE	77.1	6.52E+06	0.808	0.1	0.0798	0.7	0.112	0.1	1.41	8.9
S0070-06-AE	81.4	5.31E+07	0.766	0.1	0.097	0.8	0.137	0.2	1.41	7.3
S0070-07-AE	85.7	9.57E+07	0.744	0.1	0.107	0.8	0.149	0.2	1.40	6.7
S0070-08-AE	90.0	5.55E+05	0.995	0.04	0.002	10.0	0.0032	10.7	1.48	316
Water Extracts										
S0070-03-WE	68.4		0.656	2.6	0.151	1.7	0.193	10.3	1.27	5.18
S0070-03-WE-Rep	68.4		0.638	2.2	0.155	8.1	0.206	2.6	1.33	4.85
S0070-06-WE	81.4		0.627	1	0.150	5.3	0.223	6.1	1.49	4.49
S0070-07-WE	85.7		0.622	0.6	0.157	1.6	0.222	1.1	1.42	4.51
Model Prediction									1.21	4.52

Table D.6.1.3. Cesium Isotopic Measurements on Samples
From Long-Term Electrolyte Leaching Experiments.

Sample ID	Sample Name	Cs-133 Ug/L	Cs-133 Abundance	Cs-135 Abundance	Cs-137 Abundance	Cs-137/ Cs-133 Ratio	Cesium/ Cs-137 Ratio
57487-35-3	SX-108-07A	5.95	0.634	0.152	0.214	1.403	4.68
57487-38-3	SX-108 03A	3.50	0.655	0.144	0.202	1.403	4.96
57487-41-3	41-09-39 7A/B/C	3.68	0.636	0.148	0.216	1.467	4.62

D.6.1.3.2 Molybdenum Isotopes. Mo is one of the more isotope rich elements in the periodic table with a total of seven stable isotopes amenable to mass spectrometric analysis (92, 94, 95, 96, 97, 98, and 100). Four of those isotopes are fission products resulting from beta decay of neutron rich high-yield parent isotopes (95, 97, 98, and 100). The other three can be produced in very low yields as direct fission products, but since all three are blocked from the beta chain by stable isotopes of Zr, cumulative fission yields are negligible. Mo isotopes at masses 92, 94, and 96 can be regarded as essentially invariant in composition and representative of naturally occurring Mo. ^{95}Mo is an intermediate case since it has two radioactive precursors with moderately long half-lives, ^{95}Zr (64.02 days) and ^{95}Nb (34.97 days). ^{95}Zr , in particular, is likely to have survived the cool-off period in sufficient quantity prior to REDOX processing to be significant. Thus, some degree of chemical separation is likely to have perturbed the isotope ratio to a lower value *than* that shown in Table D.6.1.1. This effect provides a means to discriminate between different sources because compositions will depend on the inevitable variations in cool-off time and processing chemistry. Measured Mo isotope ratios from water leaches on SX-108 core material support that premise. Table D.6.1.4 lists the measured isotopic compositions of the water leach samples. Measurements were also performed on the acid leach samples; however, it ~~was~~ clear from the screening results that the large quantity of naturally occurring Mo leached out of the sediment obscured the fission product signal. By contrast, the Mo in the water leaches ~~was~~ dominated by a fission-derived component accounting for up to 96% of the total Mo at the maximum concentration. Table D.6.1.4 shows the composition of natural and purely fission derived Mo compositions across the top two rows for comparison.

Figure D.6.1.2 shows two different representations of the distribution of Mo isotopes in the S-X108 core as a percentage derived from fission. The top plot compares the total Mo concentration measured by ICP-OES with the mass spectrometric determination of fission-derived ^{100}Mo expressed as a percentage associated with fission. The bottom plot shows the same calculation for all four fission-derived isotopes. It is quite clear that the effect of separate events is more readily discernable using the fission-derived isotopes. Three fission-containing peaks are clearly evident with maxima at 68 feet, 90 feet, and 116 feet. The shallowest and deepest peaks contain much less total fission Mo so the percent fission component is somewhat less, however, the fission component still represents more than 80% of the total Mo even in the smaller peaks.

**Table D.6.1.4. Molybdenum Isotopic Composition in Water Extracts
From SX-108 Slant Borehole Core Segments.**

Sample ID	Vertical Depth in Core Feet BGS	Mo-92 0.148 0.000 Abund.	Mo-94 0.0925 0.000 Abund.	Mo-95 0.159 0.255 Abund.	Mo-96 0.167 0.000 Abund.	Mo-97 0.0955 0.243 Abund.	Mo-98 0.241 0.239 Abund.	Mo-100 0.0963 0.263 Abund.	Natural Fission
S0070-01 A	55.4	0.141	0.087	0.163	0.162	0.103	0.245	0.099	
S0070-01 A DUP	55.4	0.140	0.087	0.165	0.159	0.102	0.243	0.105	
S0070-03 A	68.4	0.040	0.025	0.225	0.046	0.203	0.244	0.217	
S0070-04 A	72.7	0.090	0.055	0.197	0.100	0.155	0.241	0.161	
S0070-05 A	77.1	0.043	0.026	0.226	0.047	0.202	0.243	0.213	
S0070-06 A	81.4	0.017	0.008	0.242	0.014	0.229	0.244	0.246	
S0070-07 A	85.7	0.015	0.008	0.243	0.014	0.231	0.243	0.246	
S0070-08 A	90.0	0.108	0.013	0.217	0.021	0.204	0.222	0.213	
S0070-09 A	94.4	0.108	0.013	0.217	0.021	0.204	0.222	0.213	
S0070-10 A	98.7	0.408	0.049	0.120	0.085	0.086	0.163	0.089	
S0070-11 A	103.3	0.148	0.092	0.160	0.165	0.096	0.239	0.099	
S0070-12 A	107.3	0.150	0.093	0.163	0.167	0.094	0.239	0.094	
S0070-13 A	116.0	0.090	0.022	0.218	0.039	0.196	0.229	0.206	
S0070-14 A	124.7	0.288	0.062	0.143	0.110	0.100	0.196	0.101	
S0070-14 DUP A	124.7	0.312	0.056	0.140	0.100	0.100	0.188	0.104	
S0070-15 A	133.3	0.359	0.069	0.121	0.122	0.072	0.182	0.074	
S0070-16 A	142.0	0.154	0.094	0.164	0.162	0.096	0.235	0.094	
S0070-17 A	148.9	0.159	0.094	0.163	0.164	0.095	0.235	0.090	

Figure D.6.1.2. Fraction of Total Molybdenum Derived from Fission.

Since both peaks are heavily dominated by a fission component, it is possible to use the non-fission derived isotopes (92, 94, and 96) to correct for the natural component present in each core segment leachate and calculate a composition for the purely fission-derived components. Table D.6.1.5 lists the calculated isotopic ratios for the fission-only component for the three peaks with the contribution from naturally abundant Mo stripped out. Isotopic ratio precision is typically around 1% relative or less; however, only the middle peak was wide enough to calculate a relative error directly on multiple segments. These data indicate three distinctly different sources of fission product containing waste.

Depth (feet)	100/98	97/98	95/98
81 to 90	1.078	0.997	0.917
+/-	0.008	0.009	0.011
%RSD	0.7%	0.9%	1.2%
116	1.083	1.012	0.758
Model	1.100	1.010	1.06

Mo is almost certainly present in tank supernate as the Mo oxyanion. Mo falls beneath Cr in the periodic table and should function in a geochemical system as a surrogate for hexavalent Cr with the primary chemical difference being that hexavalent Mo is less easily reduced to the trivalent form than is the case for hexavalent Cr. Figure D.6.1.3 shows a comparison between Cr and Mo measured in the core water extracts by ICP-OES (Serne et al. 2001c). As demonstrated above, the Mo in the water leaches is dominated by a fission component originating from tank supernate while the Cr is associated with chemical additives from the REDOX process found in major quantities in tank supernate. Both species show evidence of three separate events with the three Mo peaks retarded relative to the three corresponding Cr peaks.

Figure D.6.1.3. Fraction of Total Chromium and Molybdenum in SX-108 Water Extracts.

Cr itself appears to be significantly retarded in its vertical transport relative to Tc. Tc along with chloride, nitrate, sulfate, and tritium functions as a purely conservative, unretarded tracer in this system. Figure D.6.1.4 compares the distribution of Cr and ^{99}Tc in water extracts with the Cr peaks clearly shifted to shallower depths. The retardation of both Cr and Mo appears to be associated with either sorption or precipitation on a solid phase. Figure D.6.1.5 shows the comparison between water and acid extracts for Cr. A substantial fraction of the total Cr is unavailable for extraction by water. While it was not possible to perform the same experiment directly for Mo because of the substantial natural component in the acid extracts, it is reasonable to infer that an even larger fraction of the Mo is tied up in a solid phase based on the greatly reduced peak height for the lower fission peak at the 16 feet depth. Except for differences in peak height and minor differences in retardation, the Cr and Mo appear to behave similarly. It is likely that the loss of water-extractable Cr is not a REDOX effect because Mo is less easily reduced than Cr. The loss is more probably associated with co-precipitation with an indeterminate solid phase.

Figure D.6.1.4. ^{99}Tc and Cr in Water Extracts From SX-108 Core.

Figure D.6.1.5. Chromium in Water and Acid Extracts From SX-108 Core.

D.6.1.3.3 Iodine Isotopes. ^{129}I is a fission product with a medium yield (0.54%). A great deal of attention has been focused on the two radioactive isotopes of I (131 and 129) in recent years because of their tendency to accumulate in the thyroid. Radio-iodine is thus considered a very hazardous substance when released to the environment with correspondingly stringent regulatory limits (drinking water standard = 1 pCi/L for ^{129}I). Because it is typically present in anionic form as iodide, I also tends to exhibit high environmental mobility although some minor retardation is

possible under some conditions (Kaplan and Serne 1995). Under the strongly oxidizing conditions present during fuel dissolution, I is generally believed to be released as elemental I. During operation of REDOX, it thus tended to partition heavily into the vapor phase where it was either released as stack emissions, collected on silver vapor traps, or accumulated in process condensate for eventual release through the groundwater pathway. Very little ^{129}I is thus expected to be present in tank waste; however, any residual fission-derived I disposed to tanks is likely to be found almost exclusively in the supernate and available to be released in association with leaks. Stable I (^{127}I) also should be present in nuclear waste to some degree either through use of I as a reducing agent in REDOX or simply as a chemical impurity. In any case, irrespective of its chemical source, the ^{127}I to ^{129}I ratio in tank waste is likely to be very widely variable constituting an ideal signature for individual waste streams.

^{127}I and ^{129}I measurements on the water extracts from the SX-108 cores are reported in Table D.6.1.6. The depth profiles for the two I isotopes are plotted in Figure D.6.1.6. Two peaks are clearly discernable in the vertical depth profile with a very large difference in the relative amounts of ^{127}I vs. ^{129}I in the two peaks. On a relative basis, the peak at lesser depth has almost twice as much stability I as does the peak lower in the core. These two peaks unquestionably represent material from different sources.

Figure D.6.1.6. Iodine Isotopic Distribution in Water Extracts From SX-108 Core.

**Table D.6.1.6. ^{127}I and ^{129}I in Water
Extracts From SX-108 Core.**

Sample ID	Vertical Depth in Core (Feet BGS)	^{129}I $\mu\text{g/L}$	^{127}I $\mu\text{g/L}$
S0070-01 A	55.4	< 0.17	12.6
S0070-01 A DUP	55.4	< 0.21	14.0
S0070-03 A	68.4	0.39	11.6
S0070-04 A	72.7	0.39	9.2
S0070-05 A	77.1	1.20	23.1
S0070-06 A	81.4	8.70	62.5
S0070-07 A	85.7	14.3	194
S0070-08 A	90.0	14.5	211
S0070-09 A	94.4	15.9	89.8
S0070-10 A	98.7	24.1	122
S0070-11 A	103.3	1.07	18.0
S0070-12 A	107.3	1.30	31.5
S0070-13A	116.0	15.8	74.1
S0070-14 A	124.7	15.0	90.9
S0070-14 DUP A	124.7	16.5	101
S0070-15 A	133.3	21.2	179
S0070-16 A	142.0	1.48	27.9
S0070-17A	148.9	0.72	13.5

Figure D.6.1.7 shows a comparison between the concentrations of ^{129}I and ^{99}Tc as measured in the same water leachate samples. The ^{129}I data plotted on the figure **has** been renormalized by the ratio of fission yields between ^{99}Tc (6.1%) and ^{129}I (**0.54%**). When plotted in that way, it is possible to make a direct estimate of I losses during REDOX chemical processing for the two peaks. A simple comparison of the two plotting axes reveals that more than 98% of the I was lost relative to the Tc. However, both peaks **look** otherwise similar when viewed in that way. In order to convincingly demonstrate that two sources are present, it is necessary to include the ^{127}I , which forms a kind of internal tracer showing the major difference in composition between the two peaks. It should also be noted that Figure D.6.1.7 demonstrates that I does exhibit some minor retardation relative to unretarded ^{99}Tc .

Figure D.6.1.7. Iodine and ^{99}Tc Comparison in Water Extracts From SX-108 Core.

D.6.1.3.4 Selenium Isotopes. Like ^{129}I , ^{79}Se is also formed as a medium yield fission product with a potentially high environmental mobility. The half-life of ^{79}Se has seldom been measured, with the currently accepted value of 1.13 million years based on a recent determination involving accelerator mass spectrometry combined with liquid scintillation counting performed in the Peoples Republic of China (Songsheng et al. 1997). Because of analytical difficulties associated with routine direct measurement of ^{79}Se , little is known about its distribution in the environment. Se can form an oxyanion, selenate, which is likely to be highly mobile. ^{79}Se is often cited as one of the critical path long-lived radionuclides used for performance assessment of tank waste removal and for risk assessment of tank leaks. ^{79}Se and other naturally occurring and fission-produced isotopes (74, 76, 77, 78, 80, and 82 amu) can in principle be measured by ICPMS; however, measurement of the full suite of isotopes is rendered difficult by an abundance of interferences in that mass region. Because of time and budget constraints associated with issuance of this report, the needed development work could not be completed. However, it is possible to estimate the mobility of fission-derived Se using one of the other fission-produced stable isotopes of Se. Stable ^{82}Se is produced with a fission yield about 5 times higher than that of ^{79}Se . Since ^{82}Se also represents 8.7% of naturally occurring Se, conclusions derived from ^{82}Se alone must be considered as tentative. Figure D.6.1.8 shows the measured ^{82}Se in water leaches from the SX-108 core compared to ^{99}Tc measured on the same samples. The Se data plotted on the figure has been renormalized to the ^{99}Tc fission yield and plotted on the same axis. When plotted in that way it is clear that the two species behave essentially in an identical manner and are completely unretarded. The low baseline at the shallower depths indicates that there is very little natural Se leached out of the core material in the water extracts. The shape of the profile requires that the observed Se originates from the tank and its close agreement to the ^{99}Tc levels after correction for fission yield suggests this is almost certainly fission derived material. An identical situation was also observed in the 41-09-39 borehole associated with the tank SX-109 leak.

Figure D.6.1.8. ^{82}Se and ^{99}Tc Comparison in Water Extracts From SX-108 Core.

The ^{79}Se concentrations in the water extract samples can be inferred from the ^{82}Se , assuming no natural contribution to the ^{82}Se , by using the ratio of the ^{235}U fission yields. Table D.6.1.7 shows the inferred concentration of ^{79}Se in the water extract samples as well as the concentration converted to pCi/L of extract (using a specific activity of $4.01\text{E-}3$ Ci/g).

Table D.6.1.7. ^{79}Se Concentrations Inferred From Stable Fission Derived ^{82}Se in Water Extracts from the SX-108 Core.

Sample #	Depth(ft) Vertical	mg/L ICP/MS ^{82}Se	mg/L Inferred ^{79}Se	pCi/L Inferred ^{79}Se
S0070-01A	55	0.000	0.0000	0
S0070-03A	68	0.051	0.0072	28709
S0070-04A	73	0.050	0.0070	28194
S0070-05A	77	0.007	0.0010	3835
S0070-06A	81	0.048	0.0067	26915
S0070-07A	86	0.061	0.0085	34263
S0070-08A	90	0.149	0.0210	84029
S0070-09A	94	0.132	0.0185	74289
S0070-10A	99	0.165	0.0231	92781
S0070-11A	103	0.121	0.0170	68261
S0070-12A	107	0.008	0.0011	4510
S0070-13A	116	0.243	0.0342	137017
S0070-14A	125	0.233	0.0328	131595
S0070-15A	133	0.411	0.0578	231766
S0070-16A	142	0.031	0.0044	17729
S0070-17A	149	0.014	0.0019	7664

D.6.1.3.5 Chloride, Nitrate, Sulfate, and Technetium. Isotopic data can provide the most definitive basis for source attribution since no assumptions are needed with respect to chemical effects. However, a number of species are known or believed to migrate in the vadose zone in an almost purely unretarded fashion. Under those conditions, concentration ratios of species with similar or identical geochemical behavior can also be an effective means for identifying sources. Species well suited to that purpose include chloride, nitrate, sulfate, and ^{99}Tc . Data for the common anions discussed here were taken from the work of Serne et al. (2001c), while the ^{99}Tc measurements were made on samples from the same leachates provided by that group. Figure D.6.1.9 shows the distribution of nitrate and chloride in the SX-108 slant borehole core. It is clear that these two distributions are markedly different. It is interesting to note that nitrate exhibits a small degree of retardation in the upper peak. That behavior is unexpected and the cause is not obvious.

D.6.1.4 Conclusions and Implications

Tank SX-108 was placed in service in late 1958 for disposal of REDOX Process high-level waste. The tank began self-boiling in mid-1959 and was completely filled with self-boiling waste by early 1959. The first evidence of unaccounted volume loss and other indications of a potential leak were first noted in the third quarter of 1962 (WHC 1992). Contaminants found in the deepest part of the SX-108 slant borehole thus presumably date from some time prior to that date. The tank was emptied in 1962 and left dry for about a year. Prior to refilling, condensate from another tank was used to recover sodium nitrate salt cake from tank SX-108. It is now considered quite likely that the leak which had self-healed reopened as a result of dissolution of the salt plug at that time. Tank SX-108 was then filled with another round of fresh REDOX waste from mid-1963 through the end of 1964. Because of concerns raised by increasing activity in lateral wells in November 1965, an isolation cooler was added to the tank which was then shifted to total reflux operation in order to stabilize the liquid level. Stable behavior was subsequently noted suggesting that the leak had again self-healed. Estimates of the volume of leaked material vary widely. The best estimate based on ^{137}Cs data is around 2,400 gallons (Raymond and Shdo 1966) with an upper bound in the range of 35,000 gallons. There is good evidence from the historical record that a significant volume of material representing two different fills was leaked over a relatively long period of time at that location. Measurements conducted on recovered materials from the SX-108 slant borehole, drilled through the heart of the leak plume show evidence to support that scenario.

The best evidence for multiple leak events is visible in the ^{129}I data, which shows a very large difference in isotopic composition of I isotopes between the two concentration maxima in the core. The ^{127}I to ^{129}I ratio thus appears to be an excellent fingerprinting tool for determining source attribution. ICPMS proved in this study to be a very powerful tool for rapid and low-cost analysis of ^{129}I and ^{127}I on radioactive samples.

The slight sorption of ^{129}I implied by the comparison of the ^{129}I profile to that of ^{99}Tc is in at least general agreement with experimental results (Kaplan and Serne 1995). Application of the experimental results is complicated by the widely varying K_D values reported. This variability may be related to a strong nonlinearity in the sorption isotherm. Because iodide is an anion, the sorption may be controlled by a small number of positively charged sites on the edges of clays and on I and Al oxide surfaces. Thus, the sorption sites may be easily saturated. Competition with other anions may also be a factor.

Mo isotopic analysis also looks promising as an isotopic fingerprinting tool. Variability in the ^{95}Mo to ^{98}Mo ratio from tank to tank provides an excellent means for distinguishing separate sources. Three separate sources of material are indicated in the SX-108 slant borehole corresponding in all likelihood to the first filling in the early 1950s, the second filling in the 1962 to 1964 time frame, and possibly a later leak which occurred in the late 1960s. Mo isotopes also look promising as tracers of tank leak material into groundwater where such impacts are known or suspected, however, because of the high background of naturally occurring stable Mo normally found in groundwater, high precision mass spectrometric techniques would be needed. Recent advances in the development of multicollector ICPMS instruments make the approach very practical.

Se appears to be essentially unretarded under conditions within the Hanford sediments of the SX tank farm. Although early experimental evidence indicated that the K_D value is near zero under anoxic as well as oxic conditions and at both low and high ionic strengths (Kaplan and Seme 1995), more recent experiments showed a measurable K_D for Se in Hanford formation sediments from the 200 East Area. Kaplan et al. (1998) obtained Se K_D values of 6.73 with a standard deviation of 1.9 using ^{75}Se spiked, uncontaminated Hanford groundwater. Under the study conditions, no sorption was seen for ^{99}Tc . Kaplan et al. (1998) also studied the effect of **high** ionic strength and high pH on Se sorption to 200 East Area sediment. They found that increasing ionic strength increased sorption of Se from a K_D of 3.31 mL/g in 0.05 M NaClO_4 to 4.49 in 0.10 M NaClO_4 and 4.11 in 1 M NaClO_4 . Increasing pH from 8.1 to 9.9 decreased the Se K_D from 5.78 mL/g to 0.29 mL/g and the value decreased further to 0.04 mL/g at pH 11.9. It is important to note, however, that in these experiments the K_D for ^{99}Tc increased from -0.02 mL/g at pH 8.1 to 1.04 to 1.07 mL/g at pH 9.9 and above.

The increasing Se K_D but decreasing Tc K_D seen with increasing pH in the Kaplan et al. experiments suggests that the pH effect does not explain the Se mobility at the SX tank farm. The correlation between ^{82}Se and ^{99}Tc at the tank farm would most likely not continue as contaminants moved to greater depths and lower pH. More work is needed to understand this discrepancy between field and experimental data. Until this is better understood, caution should be used in applying the experimental results in contaminant transport and risk calculations. Because of the long half-life and high mobility, the presence of ^{75}Se should be considered in long-term risk calculations for the tank farms. ^{75}Se activities are only approximately 0.01 to 0.02 times the ^{99}Tc activity in the most concentrated water extracts, however biological uptake of Se may affect the relative risk.

Se isotopes show promise as contaminant tracers because fission-produced ^{82}Se associated with tanks leaks from SX-108 and SX-109 was found to be completely unretarded with mobility identical to that of ^{99}Tc . Some additional improvements in ICP/MS methodology are needed to measure the radioactive species, ^{75}Se , directly.

The Cs isotopes showed remarkably constant isotopic composition on water and electrolyte leaches. The presence of separate leak sources clearly visible from several other lines of evidence was not discernable from the Cs data in spite of an expected large variability in ^{135}Cs concentration predicted from nuclear modeling considerations. A more extensive series of Cs measurements is needed to better define the range of variability. Very minor amounts of naturally occurring Cs at most were leached by month-long exposures to concentrated sodium nitrate solutions. The observed ^{135}Cs in the leachates was attributable to an essentially pure fission component. Those data can be used to correctly assess the total Cs loading in sorption experiments and transport calculations.

An example of the use of fingerprinting techniques is shown in Table D.6.1.8. The table contains comparisons of the ratios of several different unretarded species. Data in the table are taken from (Seme et al. 2001a, b, c) as well as employing the I and Tc data reported above. The two SX-108 columns represent the two different peak maxima with SX-108-A associated with the earlier leak (deeper in core) and SX-108-B the more recent one. The SX-109 column refers to measurements made on the 41-09-39 borehole. Well 299-W23-19 is a Hanford groundwater well completed from the B8809 borehole drilled to measure contaminants

associated with the tank SX-115 leak. Contamination by even the most mobile constituents in the recovered core from the borehole tails off more than 50 feet above the surface of the water table; however, substantial contamination indicative of presumptive tank leak material was observed in groundwater at the completed well. ^{99}Tc in this well is extremely high at 72,300 pCi/L as measured in December 2000. Unfortunately, Table D.6.1.8 contains several key data gaps since ^{129}I was not measured in the borehole samples. While ^{129}I was measured by a gamma counting method on a sample from the well, the method does not yield an isotope ratio. Nevertheless, even from the limited data set available, it is clear that each of the sources is distinct from each other. For example, while the nitrate to Tc ratio is very similar in both the well and borehole, the nitrate to chloride ratio is very different. This suggests that the groundwater impact observed at well 299-W23-19 is not associated with the tank SX-115 leak itself but rather a leak from one of the other SX tank farm sources conveyed by some type of preferential pathway to that location. Similarly, the three ratios measured in the groundwater sample are also a poor match to the SX-108 and SX-109 samples. In order for fingerprinting techniques to achieve their full potential, more comprehensive analyses need to be performed on a wider suite of samples.

Table D.6.1.8. Contaminant Fingerprints in Water Extracts and Groundwater.

	SX-108-A	SX-108-B	SX-109	299-W23-19	B8809
NO_3/Cl	104	360	118	37	121
Tc-99/I-129	56	57		134	
$\text{NO}_3/\text{Tc-99}$	50,934	92,547	60,381	158,991	169,526
I-127/I-129	13.8	24.4			

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D.6.2 HORIZONTAL TRANSPORT OF CHEMICAL WASTE INFERRED FROM ISOTOPIC AND CHEMICAL MEASUREMENTS OF CORE SAMPLES FROM B8812 CLEAN BOREHOLE

D.6.2.1 Introduction

Understanding the mechanisms and pathways of water movement through the vadose zone at Hanford is clearly necessary for evaluating the potential for contaminant transport at the Site. To address this issue for the S and SX tank farms, an isotopic and chemical study of porewater samples from the B8812 “clean” borehole was undertaken.

The stable oxygen ($\delta^{18}\text{O}$) and hydrogen (δD) isotopic compositions of water provide natural labels for water (e.g., Epstein and Mayeda 1953; Friedman 1953; Craig 1961). In addition, evaporation modifies the isotopic signature of water, producing a distinctive signal that can be used to track the affected fluids (e.g., Gat et al. 1969; Gaye and Edmunds 1996). In the area of the S and SX tank farms, the potential inputs to the vadose zone porewaters (local precipitation, process waters derived from the Columbia River) have $\delta^{18}\text{O}$ and δD values in the same range as the groundwater. However, evaporation appears to have significantly affected most of the vadose zone waters in the area.

D.6.2.2 Experimental Procedures

The B8812 borehole was drilled in October 1999 and the cores were stored at 4 °C in sealed sleeves to prevent evaporation until they could be sampled for isotopic analyses. During January 2000, 32 samples were collected from the core. The porewaters were extracted from these samples by vacuum distillation at the Center for Isotope Geochemistry (CIG) at LBNL. The amount of water in each of the samples was determined gravimetrically. The $\delta^{18}\text{O}$ values of the porewaters were analyzed using the automated $\text{H}_2\text{O}-\text{CO}_2$ equilibration system on CIG's VG Prism Series II Isotope Ratio Mass Spectrometer. The δD values of the porewater samples were measured by reducing the water to H_2 gas with zinc metal and analyzing the isotope ratio of the resulting gas with Prism (Vennemann and O'Neil 1993). Chemical analyses of the porewaters were done using 1:1 deionized water leaches of the core material.

D.6.2.3 Results

D.6.2.3.1 Isotope Data. The $\delta^{18}\text{O}$ values of the porewaters are plotted versus their δD values on Figure D.6.2.1. Also plotted on this figure are isotope data for Hanford groundwater samples analyzed in this laboratory, the Global Meteoric Water Line, the Local Meteoric Water Line determined by Hearn et al. (1989), and a characteristic trend for evaporated water. The groundwater samples cluster around the Local Meteoric Water Line. With several notable exceptions, the porewater samples are all shifted to the right of the Local Meteoric Water Line, indicating that these waters have undergone significant evaporation.

Figure D.6.2.1. Plot of δD vs. $\delta^{18}O$ Values for Pore Water Distilled From Samples of the B8812 Core (black circles) and Groundwater Samples From Across the Hanford Site (open circles).

Note: Also shown are the Global Meteoric Water Line, the Local Meteoric Water Line (Hearn et al. 1989) and a Characteristic Evaporation Trend.

The oxygen isotope data for the porewaters are plotted versus depth in Figure D.6.2.2. The $\delta^{18}O$ value of the shallowest sample (taken at approximately 0.5 m depth) is much higher than either local precipitation or process water derived from the Columbia River (the two potential sources of surface water), signifying that it is strongly evaporated. This is typical of near-surface soil waters, especially in arid and semiarid environments. At 2 m depth, however, the $\delta^{18}O$ value of the porewater is equal to the average value of precipitation/Columbia River water. Beneath 2 m, most of the porewaters are shifted to higher $\delta^{18}O$ values, implying that they have also been evaporated. There were two porewater samples from the deeper part of the core that did not have an evaporated signal (the 44.7 and 71.8 m samples). The deeper sample is from the saturated zone and essentially reflects the isotopic composition of the groundwater. The other sample is from a perched water zone above the caliche layer in the core.

Figure D.6.2.2. Variation with Depth of the $\delta^{18}\text{O}$ Values of the Pore Water Samples Distilled From the B8812 Core.

Note: Also shown are the approximate depths of the Perched Water Horizon (underlain by a 60-cm-thick caliche layer) and Groundwater.

D.6.2.3.2 Chemical Data. Chemical measurements by ion chromatography and ICP/MS performed on water leachates from the B8812 core also showed a signature associated with perched water layer at the Plio-Pleistocene boundary. Figure D.6.2.3 shows a plot of nitrate and sulfate concentrations in 1:1 water leaches compared with the associated $\delta^{18}\text{O}$ values for the same core horizons.

Figure D.6.2.3. Oxygen Isotopes and Anion Concentrations in B8812 Core.

Both Se and Mo also show strong signatures at the same horizon with evidence of mobile Cr and U as well. A comparison of those data are shown on Figure D.6.2.4. Isotopic analyses for the ^{236}U and fission-derived isotopes of Mo showed no evidence of a nuclear production associated signature, however.

Figure D.6.2.4. Uranium, Chromium, Selenium, and Molybdenum Concentrations in Water Leaches From B8812 Core.

D.6.2.4 Conclusions and Implications

D.6.2.4.1 Near-Surface Samples. The isotopic compositions of the two shallowest samples (0.5 and 2.0 m depth) are significantly different than the deeper samples. The 0.5 m sample is strongly evaporated, whereas the 2 m sample is essentially equal to unevaporated groundwater/precipitation/Columbia River water. This pattern is similar to the results observed in other studies of shallow, unsaturated soils (Komor and Emerson 1994; Phillips 1995; Melayah et al. 1996; Barnes and Allison 1988). In essence, the thickness of the isotopically enriched zone is a function of the amount of infiltration and the evaporation rate. What is unique about this data set is that the samples at greater than 2 m depth also show evidence of evaporation. This implies that the upper 2 m have been impacted by a period of anomalously high infiltration that allowed unevaporated water to reach that depth. It is unlikely that this was the result of the annual precipitation cycles (wet in the winter, dry in the summer); the upper 2 m of soil contains approximately 30 cm of water and the average rainfall for this area is less than 25 cm/yr. Alternatively, it is possible that some process water was dumped on the surface at this site. B8812 borehole was drilled outside of the contaminated area, but there is anecdotal information suggesting that there was an infiltration pond for clean process waters in the vicinity (Evan Dresel, personal communication). Although there is no direct record of this activity, it is also supported by the Sr isotope ratios of the porewaters, which are in the same general range as Columbia River water (see Section D.6.3 of this report).

D.6.2.4.2 Evaporation of the Deep Vadose Zone Porewaters. At greater than 2 m depth, the isotopic compositions of all of the vadose zone porewaters (except for the perched water sample) reflect a significant degree of evaporation. The $\delta^{18}\text{O}$ values have been enriched by 2 to 4%, indicating that they have undergone 20 to 35% vaporization. Similar evaporated signatures were also observed for vadose zone porewaters collected in conjunction with tracer tests performed at the Vadose Zone Test Facility located near the 200 West Area. This implies that the Hanford vadose zone porewaters are generally evaporated.

Due to the difficulties associated with sample collection and extraction of the porewaters, there is limited data on the isotopic composition of deep vadose zone porewaters in arid and semiarid environments. Most studies on vadose zone soils have been restricted to the top few meters of the soil. In these studies, the impact of evaporation is generally limited to a thin zone (less than or equal to 0.5 m) near the surface (e.g., Komor and Emerson 1994; Melayah et al. 1996). The effect of evaporation from the surface cannot penetrate much deeper than 0.5 m because increased tension induces upward flow to balance evaporation and a steady-state isotopic profile is reached. However, if infiltration occurs normally by relatively few events (e.g., one per year penetrating to a depth of ca. 0.5 m), which then can be affected by evaporation over several months, the evaporation signature can be preserved as the water is displaced downward by succeeding infiltration events. No detailed model is available for translating the average $\delta^{18}\text{O}$ shift to an infiltration flux. However, to first order it can be reasoned that if the infiltration is episodic as suggested here, then the annual infiltration distance must be less than about 20 to 50 cm in order to produce average vadose zone water with a $\delta^{18}\text{O}$ shift of 2 to 4%. Assuming an average soil water content of 12%, this annual infiltration distance corresponds to an infiltration flux of less than 2.5 to 6 cm/yr.

D.6.2.4.3 Perched Water. The data measured for the perched water sample are of great significance for the goals of this project. Clearly, the perched water is not derived from direct, vertical infiltration in the vicinity of the borehole. The O and H₂O isotopic signatures of the porewaters above and below this horizon are distinct from the perched water. Further, the elevated levels of nitrate, sulfate, U, Mo, Se, Cr and Tc in the perched water imply that this water was derived (at least partially) from Hanford operations. The most likely candidate for the source of this water is the 216-S-3 cribs located approximately 50 m west-northwest of the borehole, although it is also possible that there could be some input from the 241-S tank farm. Understanding how these fluids reached the perched water and migrated to the location of the B8812 borehole is key to understanding how contaminants might migrate through the vadose zone.

The stable isotope data can also be used to constrain the age of the perched water. The ca. 1-m-thick perched water layer has an $\delta^{18}\text{O}$ value identical to that of Columbia River water and about 2 to 3 % different from the surrounding waters. Isotopic redistribution by combined liquid and vapor phase diffusion will dissipate this isotopic anomaly on a time scale (L^2/D) of roughly 25 years. So this perched water is almost certainly introduced recently. More detailed modeling could potentially constrain the age further.

D.6.2.4.4 Groundwater. The groundwater sample extracted from the deepest sample is also isotopically distinct from the vadose zone porewaters. As with the perched water, it is clear that natural infiltration of water through the vadose zone sediments is not a significant source of recharge. Unlike the perched water, however, there is no evidence that any contamination related to the Hanford activity has reached the groundwater at this point.

D.6.2.5 Summary

This work was restricted to uncontaminated core samples from the vicinity of the S and SX tank farms, but has some significant findings regarding the potential for contaminant transport in the area:

- Natural, vertical infiltration of water through the vadose zone, as evidenced by the pervasive evaporation of the vadose zone porewaters, is limited to less than a few centimeters per year
- Contaminants can and do migrate laterally along perched water horizons.

Analyses of the ³H (tritium) and ³⁶Cl concentrations of the porewaters and deionized water leaches from these samples could significantly enhance the results of this study. Both tritium and ³⁶Cl would help confirm whether or not the shallow porewaters and perched water were derived from Hanford process waters. ³⁶Cl data for the unaffected samples could be used to estimate vertical recharge rates in this area (e.g., Murphy et al. 1996).

D.6.2.6 References

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D.6.3 VERTICAL DISTRIBUTION OF $^{86}\text{Sr}/^{87}\text{Sr}$ ISOTOPIC RATIOS MEASURED IN B8812 CORE AND IMPLICATIONS TO WATER INFILTRATION NEAR THE SX TANK FARM

D.6.3.1 Introduction

Recent published work shows that in many instances the Sr isotopic composition of groundwater can be used to infer flow velocity and infiltration flux. This approach has been applied to groundwater at the Lawrence Berkeley National Laboratory (Johnson and DePaolo 1997a, b) at INEEL to infer locations of especially fast groundwater flow in the Snake River Plain aquifer (Johnson et al. 2000), and at Yucca Mountain to estimate infiltration flux (Marshall et al. and DePaolo et al., unpublished). The method is useful for obtaining infiltration flux estimates in situations where fluxes are small and difficult to quantify by other means, such as at LBNL and Yucca Mountain. It is also useful for establishing relative flow velocities in situations where the fluxes are very high and therefore difficult to quantify because the head gradients are very small (as at INEEL). Application of the technique requires measurements of Sr concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in fluid samples (or distilled water leaches of cores) and in rock or soil samples.

D.6.3.2 Experimental Procedures

Following the vacuum water extraction for stable isotope analysis of O and deuterium (see Section D.6.3.1), 32 soil core samples were prepared for Sr isotopic analysis. The samples were first rinsed in an amount of deionized water equal to the dry weight of the samples. The Sr contained in the rinse water is assumed to be that which was originally dissolved in the pore fluid plus any readily exchangeable Sr on the solid phases. The rinsed samples were subsequently leached with warm 8M HNO_3 and the leachate analyzed. Both the water rinse and HNO_3 leach were done according to the procedure described by ASA (1996), page 420. The Sr isotopic measurements were performed on a VG354 multi-collector thermal ionization mass spectrometer at the University of California, Berkeley; the results are listed in Table D.6.3.1.

D.6.3.3 Results

The distilled water rinse samples show a systematic down-hole shift in $^{87}\text{Sr}/^{86}\text{Sr}$ values from a high of 0.721 at a depth of 15 feet to a value of 0.712 at a depth of 185 feet. The trend of decreasing $^{87}\text{Sr}/^{86}\text{Sr}$ continues down to the local groundwater value of 0.710. There is a significant spike toward high $^{87}\text{Sr}/^{86}\text{Sr}$ at 136 feet, and smaller spikes at 56 feet and 170 feet. The Sr concentrations calculated for the porewaters are in the range 0.1 to 3.7 ppm, with the typical values being the range 1 to 2 ppm and the average value 1.4 ppm. These concentrations are higher than the typical groundwater concentration values of around 0.1 to 0.3 ppm (average of 80 samples from the 200 area is 0.24 ppm; DePaolo and Conrad, unpublished). The calculated concentrations in the vadose zone are likely to be affected by leaching of some adsorbed Sr. It is inferred therefore that the average amount of readily exchangeable Sr in the soils is about 6 times the amount dissolved in the pore water, although the range is from 1 to 20.

**Table D.6.3.1. Sr Concentration and Isotopic Results
for Core Samples From Borehole 299-W22-48.**

Interval (ft)	Depth (ft) Assigned	DI rinse $^{87}\text{Sr}/^{86}\text{Sr}^a$	DI rinse Sr/g soil (ppb) ^b	HNO ₃ leach $^{87}\text{Sr}/^{86}\text{Sr}^a$	HNO ₃ leach Sr/g soil (ppm) ^b
1.0-1.5	1.25	0.71447	664.7	0.71272	31.1
6.0-6.5	6.25	0.71529	75.0	0.71628	42.0
9.5-10.0	9.75	0.72052	41.1	0.71914	29.5
14.5-15.0	14.75	0.72098	7.7	0.71651	30.4
19.5-20.0	19.74	0.71913	37.1	0.71654	29.7
24.5-25.0	24.74	0.71913	23.9	0.71086	21.3
29.5-30.0	29.74	0.71996	41.3	0.71348	29.5
34.5-35.0	34.74	0.71817	26.4	0.71086	25.2
39.5-40.0	39.74	0.71778	75.0	0.71288	30.7
44.5-45.0	44.74	0.71767	33.7	0.71235	21.6
50.0-50.5	50.24	0.71792	69.4	0.71372	21.3
56.0-56.5A	56.24	0.71771	67.9	0.71416	23.6
56.0-56.5B	56.24	0.71930	72.7	0.71401	28.0
57.5-58.0	57.74	0.71778	70.7	0.71477	24.7
62.0-62.5	62.23	0.71755	38.3	0.71412	22.8
69.5-70.0	69.73	0.71648	20.3	0.71488	25.4
79.5-80.0	79.73	0.71648	75.0	0.71393	27.9
86.5	86.48	0.71529	52.4	0.71379	28.0
96.5	96.48	0.71495	90.5	0.71470	31.6
106.5-107.5	106.97	0.71451	49.8	0.71306	27.9
120.5	120.47	0.71567	53.6	0.71140	30.5
124.0-125.0	124.47	0.71421	42.9	0.71230	31.2
126.5-127.5	126.97	0.71774	108.0	0.71267	29.3
146.0-147.0	146.46	0.71449	134.0	0.71059	197.4
148.5-149.5	148.96	0.71529	75.0		
151.0-152.0	151.46	0.71381	100.1	0.71326	25.7
163.5-164.5	163.96	0.71374	52.7	0.71290	18.0
167.5-168.5	167.96	0.71529	71.7	0.71315	22.4
170.0-171.0	170.46	0.71312	31.2	0.71638	17.4
176.0-177.0	176.45	0.71312	31.2	0.71585	12.0
187.0-188.0	187.45	0.71225	17.1	0.71351	12.2
235.0-236.0	235.44	0.71021	13.0	0.71307	18.1

^aUncertainty is ± 0.00002 ; measured value for NBS987 standard is 0.71028

^bUncertainty $\pm 0.5\%$ of the value

The uppermost 2 samples, at depths of 1 and 6 feet, have relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ of about 0.715. The shallowest sample also has a very high Sr concentration, about 10 times the average for the rest of the core samples. The $^{87}\text{Sr}/^{86}\text{Sr}$ value of the shallowest sample is similar to Columbia River water, so the interpretation of the low $^{87}\text{Sr}/^{86}\text{Sr}$ values in the shallowest samples is that they reflect river water dumped on the surface that has been highly evaporated. The $\delta^{18}\text{O}$ data also indicate that the water was strongly evaporated. However, whereas the extreme evaporation effect is only present in the shallowest sample for $\delta^{18}\text{O}$, the two shallowest samples show the effect for Sr. **This** is expected because the high Sr concentration of the shallow water causes a small contribution from the surficial water to disproportionately shift the $^{87}\text{Sr}/^{86}\text{Sr}$ value of the underlying level.

The $^{87}\text{Sr}/^{86}\text{Sr}$ values of the nitric acid leachates are consistently lower than the values in the distilled water rinses between the depths of 10 and 165 feet. The nitric acid leaches do not represent just “exchangeable” Sr. About 5 to 10% of the total soil Sr was removed by the leaching (based on an estimated whole soil Sr concentration of 325 ppm). The strong nitric leach probably did dissolve some silicate mineral framework Sr as well as soluble phases like carbonate. The whole rock values of $^{87}\text{Sr}/^{86}\text{Sr}$ are therefore probably similar to or lower than the values in the nitric acid leaches, at least down to 165 feet, which is the approximate depth of the base of the Hanford formation. It would be desirable to measure several more analyses of nitric acid leaches nearer the bottom of the hole in the Ringold Formation. In the future, it would be more useful to treat the samples with pH-neutralized sodium acetate to determine the total exchangeable Sr content. However, even this procedure can dissolve carbonate and cause an overestimate of the exchangeable Sr content of the soils.

D.6.3.4 Model for Sr Isotopes

The overall decrease of pore fluid $^{87}\text{Sr}/^{86}\text{Sr}$ with depth in the core between 10 feet and 165 feet must be a consequence of downward percolation of pore fluids. If the pore fluid **starts** out at the surface with high $^{87}\text{Sr}/^{86}\text{Sr}$, then as it exchanges Sr with the soil during downward travel, it will gradually decrease in $^{87}\text{Sr}/^{86}\text{Sr}$. The rate of release of soil Sr to the pore fluid is effectively the mean rate of primary silicate mineral weathering, weighted by the Sr concentration and $^{87}\text{Sr}/^{86}\text{Sr}$ of the minerals (Johnson and DePaolo 1994).

If the Sr profile represents a steady-state condition, then the differential form for the depth dependence of the pore fluid $^{87}\text{Sr}/^{86}\text{Sr}$ (denoted $r_f(z)$), is:

$$\frac{dr_f(z)}{dz} = [r_s(z) - r_f(z)] \frac{R_s[\text{Sr}]_s}{v_f[\text{Sr}]_f} \quad (\text{D.6.3.1})$$

In this expression $r_s(z)$ is the bulk $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the solid at depth z , R_s is the bulk dissolution (weathering) rate of the soil at depth z , v_f is the pore velocity of the fluid at depth z , $[\text{Sr}]_s$ is the total concentration of Sr in the soil at depth z , and $[\text{Sr}]_f$ is the Sr concentration in the pore fluid plus readily exchangeable Sr at depth z . This model can be applied to the data to estimate R_s/v_f as function of depth (ratio of the dissolution rate to the fluid velocity). For this calculation, $[\text{Sr}]_{\text{soil}}$ is assumed to be a constant value of 325 ppm, based on the average values measured from about six samples of core (J. Seme, personal communication). The fluid Sr concentration is taken to be the value measured for the distilled water rinse. The $^{87}\text{Sr}/^{86}\text{Sr}$ of the nitric acid

leaches is tentatively taken to be representative of the isotopic composition of soil Sr that is released from primary weathering of the silicates and incorporated into the pore fluid as it percolates downward. The bulk soil $^{87}\text{Sr}/^{86}\text{Sr}$ may be somewhat lower than the acid leach values (analyses to check this are underway).

One question is why the fluid starts out near the surface with such high $^{87}\text{Sr}/^{86}\text{Sr}$ values. Rainwater, which has a very low concentration of Sr, probably dissolves Sr from caliche near the surface and hence initially acquires the isotopic composition of whatever is dissolved first. The Sr in the caliche may be either of aeolian origin or derived from the local soils. The shallow soil Sr can also be dominated by contributions from the weathering of biotite, which has particularly high $^{87}\text{Sr}/^{86}\text{Sr}$ (Blum and Erel 1997).

The equation above assumes that the vadose zone column is at steady state with respect to Sr isotopes. Transient disturbances to the isotope profile propagate through the section at a velocity that is equal to the fluid velocity divided by a retardation factor ($1 + m_e/m_f$), where m_e is the mass of exchangeable Sr per unit volume, and m_f is the mass of dissolved (fluid) Sr per unit volume (Johnson and DePaolo 1997a). Based on the data and typical groundwater Sr concentrations, this isotopic retardation factor is estimated to be about 7 ± 3 averaged through the 70-meter soils column. Other estimates of Sr retardation factors in Hanford soils are in the range 20 to 60 for natural fluids (based on K_d values of 5 to 15; PNNL-13037). The isotopic retardation factor can be different from the K_d -based value, because the former depends on the amount of exchangeable Sr present in the rocks, which is different from the amount that can be adsorbed in a single experiment at equilibrium.

The implication of the retardation factor is that the pore fluid Sr isotope profile represented by the deionized (DI) rinses must be a feature that dates from before Hanford operations. For a nominal pore velocity of 30 cm/yr, the transit time for perturbations through the ca. 70-meter section is greater than 1000 years for a retardation factor of 7. The exception to the steady-state assumption for the Sr profile is the upper 6 to 8 feet. Water put on the ground since 1945, if it had the signature of Columbia River water, could have caused a transient isotopic signal to propagate down section by about 5 feet. The soil column Sr isotopic ratios can however be disturbed quite easily if pre-evaporated process water is released to the ground. Since the Sr concentration in pre-evaporated water is much higher than that of river water, concentrated water can overwhelm the budget of adsorbed Sr in the soils, reducing the effective retardation to a value close to unity.

D.6.3.5 Estimates of Infiltration Flux

The available data were fit using a simple finite difference model with the equation given above (Figure D.6.3.1). The ratio R_s/v_f was taken as unknown and adjusted by trial-and-error to match the DI rinse isotopic data. The best fit was done by eye and does not attempt to reproduce every data point, but instead it represents the values of R_s/v_f that match the slope over the length scales of 10 to 40 feet. As shown in the figure, the best-fit values for R_s/v_f are in the range 0.35 to $1.2 \times 10^{-5} \text{ m}^{-1}$. This range of values could change somewhat, probably toward slightly lower values, if the bulk soil $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are significantly different from those of the nitric acid leachates.

Figure D.6.3.1. (left) Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ of DI Rinses (open circles) and Nitric Acid Leachates (solid squares) versus Depth. (right) Plot of model-derived values of R_s/v_f versus Depth.

Note: The dashed line is the best-fit trajectory for the model. The simplified lithologic column shown on the right depicts casing (white), Hanford sand (yellow), Hanford silty sand and silt (green), Ringold silty, sandy gravel (pink), clastic dikes (brown) and caliche (blue). (right) Plot of model-derived values of R_s/v_f for the best-fit model is $0.4 - 1.2 \times 10^{-5} \text{ m}^{-1}$. If the derived R_s/v_f values are changed by as much a factor of 2 in either direction, the model curve will grossly misfit the data. The model does not fit the data in the Ringold Formation or at depths below 170 feet. This misfit may be a consequence of preferential dissolution of particular minerals by the nitric acid procedure, or evidence of non-steady-state conditions.

The infiltration velocity, v_f , can be calculated if the weathering rate (R_s) can be estimated. The bulk weathering rate may be measurable using uranium isotopes, but has not yet been attempted. The rate can be estimated using studies of weathering rates of soils derived from granitic terrains in California (White et al. 1996). White et al. studied soils varying in age from 10 ka to 3000 ka. The bulk weathering rates calculated from their data, and weighted for Sr concentration are 2 to $3 \times 10^{-6} \text{ yr}^{-1}$, for soils of ages 40, 130, and 250 ka. (The bulk rate for Sr is approximately the same as the plagioclase weathering rate.) There is a slight trend of higher rates for younger soils, but there is also a trend of lower rates for deeper soil horizons, so values between 1 and $3 \times 10^{-6} \text{ yr}^{-1}$ are likely to be applicable to the Hanford vadose zone. This range of values also fits with data obtained on other soils in other studies, but the White et al. (1996) results are more comprehensive, and are most comparable to Hanford because both the mineralogy and climate are similar.

The range of R_s/v_f values of 0.4 to $1.2 \times 10^{-5} \text{ yr}^{-1}$, and $R_s = 2 \pm 1 \times 10^{-6} \text{ yr}^{-1}$, gives the estimated downward water velocity of $25 \pm 17 \text{ cm/yr}$. The average water content of the soils is about 12 volume percent, so the quoted range of velocity corresponds to an infiltration flux ($v_f \theta$) of $3 \pm 2 \text{ cm/yr}$. This value should be an average value applicable to the past 100 to 1000 years, and is not affected by any recent changes in climate or Hanford operations.

D.6.3.6 Conclusions and Implications

The objective of this study was to obtain an estimate of the average natural infiltration flux at a relatively unmodified site in the Hanford 200 Area. The Sr isotope data obtained are systematic and indicate that the infiltration flux is $3 \pm 2 \text{ cm/yr}$. The inferred flux is an average value that applies to infiltration over the past 100 to 1000 years. The implied vadose zone transit time for infiltrating waters is 300 ± 200 years for a 70-m-thick unsaturated zone with 12% average water content. This transit time applies to mobile contaminants and can be used to infer the transit time of other nuclides that are less mobile, and other areas where the vadose zone is a different thickness. The result suggests that natural infiltration is significant for moving mobile species toward the water table over hundreds of years. Similar data sets from other areas of the Hanford Site would be desirable to establish the generality of the results presented here.

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D.6.4 CONCLUSIONS OF S&T INVESTIGATIONS OF ISOTOPE GEOCHEMISTRY S-SX SEDIMENTS

A series of isotope ratio techniques were employed to investigate the premise that multiple contaminant maxima in the core represent different source materials. The best evidence for multiple leak events associated with tank SX-108 is visible in the ^{129}I data which shows a very large difference in isotopic composition of iodine isotopes between the two concentration maxima in the core. The ^{127}I to ^{129}I ratio thus appears to be an excellent fingerprinting tool for determining source attribution. ICP/MS proved in this study to be a very powerful tool for rapid and low cost analysis of ^{129}I and ^{127}I on radioactive samples.

The slight sorption of ^{129}I implied by the comparison of the ^{129}I profile to that of ^{99}Tc is in at least general agreement with previously reported experimental results. Application of the experimental results is complicated by the widely varying K_D values reported. This variability may be related to a strong non-linearity in the sorption isotherm. Because iodide is an anion, the sorption may be controlled by a small number of positively charged sites on the edges of clays and on iron and aluminum oxide surfaces. Thus the sorption sites may be easily saturated. Competition with other anions may also be a factor.

Variability in the ^{95}Mo to ^{98}Mo ratio provides an excellent means for distinguishing separate sources through isotopic fingerprinting. Three separate sources of molybdenum are indicated in the SX-108 slant borehole, likely corresponding to the first filling in the early 1950s, the second filling in the 1963 to 1964 time frame, and possibly a later leak which occurred in the late 1960s. Molybdenum isotopes also appear to work well as tracers of tank leak material into groundwater where such impacts are known or suspected. However, because of the high background of naturally occurring stable molybdenum typically found in groundwater, high precision mass spectrometric techniques may be needed; recent advances in the development of ICP/MS instruments make the approach very practical.

The Cs isotopes showed remarkably constant isotopic composition on water and electrolyte leaches. The presence of separate leak sources clearly visible from several other lines of evidence was not discernable from the Cs data in spite of an expected large variability in ^{135}Cs concentration predicted from nuclear modeling considerations. A more extensive series of Cs measurements on other tanks is needed to better define the range of variability. Very minor amounts of naturally occurring Cs were leached by month-long exposures to concentrated sodium nitrate solutions. The observed ^{133}Cs in the leachates was attributable to an essentially pure fission component. Those data can be used to correctly assess the total Cs loading in sorption experiments and transport calculations.

The fingerprinting technique was also applied to core and groundwater data from several locations in the SX tank farm. Samples included a borehole near leaking tanks SX-109 and SX-115 as well as groundwater from well 299-W23-19 near SX-115. Although only a limited data set is available, it is clear that each of the tank leak sources is distinct from each other. For example, while the nitrate to Tc ratio is very similar in both the well and borehole, the nitrate to chloride ratio is very different. This suggests that the groundwater impact observed at well 299-W23-19 is not associated with the tank SX-115 leak itself but rather a leak from one of the other SX tank farm sources conveyed by some type of preferential pathway to that location.

Similarly, the three ratios measured in the groundwater sample are also a poor match to the SX-108 and SX-109 samples. In order for fingerprinting techniques to achieve their full potential, more comprehensive analyses need to be performed on a wider suite of samples.

An assessment of the $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios in the B8812 core indicated an average water infiltration flux of 30 ± 20 mm/yr to the vadose zone over the past 100 to 1000 years. In contrast, infiltration estimates for the S and SX tank farms based on a method that uses winter precipitation and surface soil texture ~~data~~, calibrated by 20 years of Hanford lysimeter data, place the average value at 56 mm/yr with a range of 20 to more than 150 mm/yr, depending on climatic conditions. Regardless of precise value, these results suggest that natural infiltration and drainage is significant for moving mobile species (e.g., NO_3 , Cr, ^{99}Tc , $^{127/129}\text{I}$, $^{79/82}\text{Se}$) toward groundwater over time periods of decades to hundreds of years. The estimated vadose transit time for meteoric waters in the S and SX ~~tank~~ farms range from 60 to 500 years depending on assumptions and model.

D.7.0 SIMULATION OF MULTIPHASE FLUID FLOW AND REACTIVE TRANSPORT AT THE SX TANK FARM

Critical decisions on the management of wastes in the S and SX tank farms will be based on predictions of contaminant transport in the Hanford Site vadose zone. Several of these decisions will be made in the next three to five years:

- barriers to control recharge at the ground surface
- procedures for retrieval and stabilization of tank waste
- remediation of contaminated sediments.

Confidence in the model predictions is built on defensible justifications for the selection of process representations, parameters for those representations, initial and boundary conditions, as well as a demonstrated ability to capture known behaviors. Building this level of trust in the models requires a program of activities that begins with fundamental and simplified analyses that eventually lead to more comprehensive and detailed models. This section describes preliminary modeling analyses performed by the S&T Vadose Zone Modeling team to identify appropriately detailed process models for Hanford Site assessments and provide technical defensibility for their use in predicting long-term behavior of contaminants.

The S&T Vadose Zone Transport Modeling Team is part of an integrated effort to develop the understanding of contaminant behavior in the Hanford vadose zone necessary for waste management decisions. The modeling is dependent on historical data as well as ongoing studies to characterize site-specific processes and properties. These data have been or are being developed by other entities (e.g., EMSP, S&T Program, site contractors) for a variety of purposes and, in most cases, have not been examined in a comprehensive modeling framework for consistency. An important role of the modeling effort, therefore, is to identify inconsistencies between the observations and the process-level understanding, and prioritize areas that merit additional investigation.

The Modeling Team targeted the Hanford SX tank farm from three principal perspectives: (1) nonisothermal multiphase fluid flow resulting from the known temperature history of boiling waste tanks, (2) speciation of high-ionic strength tank fluids, and (3) cesium migration as a function of competitive ion exchange on Hanford sediments.

D.7.1 FLUID FLOW, HEAT TRANSFER, AND SOLUTE TRANSPORT AT TANK SX-108; A SUMMARY REPORT ON MODELING STUDIES

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D.7.1.1 Introduction

Of 15 single-shell tanks at the 241-SX tank farm, 10 are known leakers (Ward et al. 1997). Fluid flow and solute transport in the unsaturated zone surrounding the tanks is affected by radioactive decay heat and by chemical interactions between fluids and sediments. Multiphase processes near the tanks include flow of aqueous and gaseous phases, boiling and condensation, migration of solutes, precipitation and dissolution, and vapor-liquid counterflow. Additional effects arise from variable solute concentrations in the aqueous phase, heat generation from leaked radioactive fluids, interference between the heat load and fluid leaks of different tanks, and from suspected but poorly constrained water line leaks.

From an environmental management perspective, important issues at the SX tank farm include past, present, and future distribution and migration of contaminants for a “no action” scenario, as well as for various remedial measures that may be considered (such as placing covers to reduce net infiltration, or removing tank contents through sluicing). A key task for performance assessment is to predict the future rates at which different contaminants may be expected to reach the water table and enter the groundwater system. The complexity and intrinsic variability of hydrogeologic conditions and processes is such that a strictly deterministic description is not possible. Performance assessment must adopt simplified models and representations, which must be complemented by stochastic representations of uncertainties. In order to be credible and acceptable, the simplifications and approximations made in performance assessment models must be based on a sound scientific understanding of the underlying processes.

The purpose of the studies reported here is to develop a better understanding of the unique hydrogeologic system created by the Hanford tanks through detailed mechanistic modeling of fluid flow, heat transfer, and mass transport. Our aim is to provide support and guidance for performance assessment, field characterization, and decision making on remedial measures. We focus especially on tank SX-108, which is one of the highest heat load tanks in the 241-SX tank farm, and is a known leaker. A realistic quantitative model of mass and energy transport near the tanks requires

- comprehensive treatment of all significant physical and chemical processes
- accurate representation of hydrogeologic conditions at the site
- realistic parameters for fluids and sediments and for temperature and leak history of the tanks.

These are ambitious goals that can only be achieved through a process of iterative refinement, starting from relatively simple models. The initial emphasis of the work reported here is on process issues, focusing on the extent to which various multiphase and nonisothermal processes may impact the migration of moisture and aqueous solutes. We have attempted to represent significant hydrogeologic features of the Hanford sediments in a reasonably approximate way, but we have made only limited efforts to capture detailed hydrogeologic conditions at a specific tank. We have investigated a series of models that probe different processes and mechanisms, in order to determine what processes are important for contaminant behavior, and how they can be modeled effectively. The present write-up is a summary of work-in-progress; a more detailed report on our thermo-hydrologic modeling is in preparation.

D.7.1.2 Tank Effects

Emplacement of the tanks led to large changes in the hydrogeological conditions at the site. The following effects may be distinguished.

- Sediments down to approximately 16m depth were removed during construction and backfilled after tank emplacement, altering the hydrogeologic properties of the material.
- A layer of gravel and coarse sand of approximately 2 m thickness was placed on top of the tanks. This will allow precipitation to migrate more rapidly to greater depth, greatly increasing net infiltration by reducing the fraction of infiltration that can be removed by evapotranspiration.
- The “umbrella” effect of the tanks will cause infiltrating water to pond atop the tanks and be diverted sideways, with much increased water fluxes around the perimeter of the tanks.
- Due to the radioactive decay heat, temperatures in several tanks rose to well above the nominal boiling point of 100°C, in one case up to 160°C, for extended time periods. This caused elevated formation temperatures with vaporization-condensation effects and associated redistribution of moisture and solutes.
- Tank leaks can introduce hot and highly saline aqueous fluids into the subsurface, whose thermophysical properties and flow behavior may be quite different from pure water. Further changes in flow behavior could result from chemical alteration of the sediments due to reactions with the fluids.

D.7.1.3 Modeling Approach

Modeling of fluid flow, heat transfer, and mass transport at the Hanford tanks is complicated by intrinsic variability of the geologic media, and by the complex forcing of the system from natural and man-made perturbations. Important processes include water seepage from infiltration, umbrella effect and heat output of the tanks, and leakage of fluids with high ionic strength and internal heat generation. Our modeling approach borrows from techniques developed in petroleum and geothermal reservoir engineering, and mining engineering. Several different numerical simulators were used and occasionally enhanced as needed. Specific results reported here were obtained with TOUGH2 (Pruess et al. 1999).

We have simulated different cases to explore mechanisms and sensitivities. As a convenient starting point for introducing and comparing more complete process descriptions we have investigated an “isothermal reference case,” using a Richards’ (1931) equation approximation in which only the liquid (aqueous) phase is active, while the gas phase is considered a passive bystander at constant pressure. An alternative model, dubbed “nonisothermal base case,” includes tank heat effects and a comprehensive treatment of multiphase processes, including boiling and condensation, two-phase flow, and diffusion in aqueous and gas phases. Some simulations were performed to explore special effects, such as moisture tension-dependent anisotropy, and moisture redistribution from vapor diffusion that is driven by reduced vapor pressure of more saline fluids.

Each simulation case requires several (typically two) modeling segments to describe changes in boundary conditions, formation properties, and sinks and sources from tank construction and from storage and leakage of waste fluids. The modeling process begins with the calculation of a “natural state” that corresponds to hydrogeologic conditions prior to tank construction. The natural state entails steady flow (gravity-capillary equilibrium) under conditions of uniform and time-independent infiltration at a rate of 1 cm/yr at the land surface. Subsequent emplacement of tanks was modeled by using the previously calculated steady state conditions as initial conditions, and making the following changes in the model:

- modify hydrogeologic parameters in the regions occupied by tank and backfill
- alter evapotranspiration conditions at the land surface to a net infiltration of typically 10 cm/yr (Gee et al. 1992)
- introduce appropriate time-dependent sources of heat and saline fluid to model radioactive decay heat and fluid leakage from the tanks.

The starting time of the tank simulations is 1955 (1955.82 to be precise), which is the beginning of monitoring data for tank SX-108. Land surface infiltration at a rate of 10 cm/yr includes a small amount of conservative solute tracer, arbitrarily modeled as 0.1 wt% NaCl, which was added to facilitate monitoring the downward advance of infiltration. Heat generation from the tank is modeled by specifying actual measured tank temperatures as time-dependent boundary conditions on the tank surface. A tank leak was also investigated, see below.

The 241-SX tank farm includes 15 single-shell tanks that are placed in a regular pattern in 5 rows and 3 columns (Conway et al. 1997; see Figure D.7.1.1) with 30.4 m spacing between tank centers (Piepho 1999). To simplify the analysis we consider the vertical planes that bisect the lines between tank centers as planes of symmetry. This will only be approximately valid even for the centrally located tank SX-108, because of different heat loads from different tanks and intrinsic variability in hydrogeologic properties. However, this simplification is appropriate for a study that focuses on coupled multiphase fluid and heat flow effects. It greatly facilitates the analysis, because it is only necessary to model the shaded region in Figure D.7.1.1, with “no flow” conditions applied at the lateral boundaries. For this initial study we make a further approximation and replace the rectangular model domain by a cylinder with radius chosen in such a way as to preserve the cross-sectional area, i.e., $\pi R^2 = 30.4 \times 30.4 \text{ m}^2$, so that $R = 17.15 \text{ m}$. The simulation model then simplifies to a two-dimensional R-Z section (radius-depth).

Geometric parameters used in the model were obtained from a construction diagram of tank SX-108.

Figure D.7.1.1. Plan View of the 241-SX Tank Farm, After Conway et al. (1977).

Note: The shaded region around tank SX-108 indicates an approximate symmetry domain.

The dominant hydrogeologic feature at the Hanford Site is the layered structure of the sediments, which is due to the depositional history from a series of cataclysmic floods. However, texture, permeability, and porosity of the individual hydrogeologic units is far from uniform. An intensive program of field sampling and testing, and laboratory analysis, has revealed considerable heterogeneity within individual hydrogeologic units, with permeabilities of bench-scale specimen typically varying over 3 to 4 orders of magnitude (Khaleel and Freeman 1995; Khaleel et al. 1995; Khaleel and Relyea 1997; Smoot and Lu 1994; Rockhold 1999; Khaleel et al. 2000). The predominant large-scale layered structure of the Hanford sediments is significantly disturbed on a local scale; for example, a sloping layer of coarser material has been identified beneath tanks SX-108 and SX-109 (Price and Fecht 1976; Khaleel et al. 2000). Additional complications arise from the presence of clastic dikes. These form extensive networks of sub-vertical structures that could play a role in generating localized preferential flow.

The approach taken in this work is to start from a simplified representation of hydrogeologic structure that honors large-scale layering. In the initial phase of this project our emphasis is primarily on a systematic exploration of process-related issues, e.g., coupling between fluid flow, heat transfer, solute transport, and chemical changes. As our understanding of process-related issues and applicable parameters improves, we intend to introduce more specific hydrogeologic features known to exist near tank SX-108 in step-wise fashion. In the present work, the formation is modeled with "layer-cake" stratigraphy, as shown in Table D.7.1.1 and Figure D.7.1.2. A summary of parameters used for the reference case is shown in Table D.7.1.2. Additional parameter specifications needed for two-phase nonisothermal effects and mass transport are given in the full report (Pruess et al. in preparation). Work is ongoing to explore parameter sensitivities and to implement more site-specific hydrogeologic detail.

**Table D.7.1.1. Stratigraphic Sequence at
241-SX Tank Farm, After Ward et al.
(1996).**

Unit	Thickness	To depth
Backfill	15.4 m	15.4 m
Hanford fine sand	23.6 m	39 m
Plio-Pleistocene	6 m	45 m
Upper Ringold	3 m	48 m
Middle Ringold	20 m	68 m

**Figure D.7.1.2. Model Domain Showing Stratigraphic Units (a)
and Computational Grid (b).**

Table **D.7.1.2.** Formation Parameters for Reference Case (Richards' Equation).

Formation parameter		Backfill	Hanford	Plio-Pleistocene	Upper Ringold	Middle Ringold
Permeability (m ²)	hor.	2.48e-12	3.70e-13	4.10e-14	1.58e-13	2.20e-13
	vert.	1.24e-12	1.23e-13	1.37e-14	0.53e-13	0.73e-13
Porosity		0.2585	0.3586	0.4223	0.2625	0.1643
Liquid rel. perm.	m	0.658	0.469	0.456	0.386	0.392
	S _{lr}	0.0774	0.0837	0.2595	0.2130	0.0609
Cap. pressure (1/Pa)	$\alpha/\rho g$	10.08e-4	9.394e-5	6.841e-5	2.961e-5	6.331e-5

The computational grid as shown in Figure D.7.1.2 has 22 blocks in R-direction and 44 layers, for a total of 968 grid blocks. The entire tank volume is included in the discretization domain but is omitted from Figure D.7.1.2b. The region occupied by the tank is assigned zero permeability in the simulations, except of course in the natural state (pre-emplacement) simulations where it is given properties identical to the backfill domain. Radial grid increments are $\Delta R = 1$ m near the tank center, decrease to 0.53 m near the perimeter of the tank, and then increase to 0.98 m at the outer boundary of the model domain. Vertical thickness of grid layers varies from 0.33 to 4 m. Finer gridding is used near the land surface, near the bottom of the tank, and at lithologic contacts.

For the pre-emplacement state we adopt boundary conditions of 1 c d y r net infiltration at the top, and a water pressure of 1.405 bar at the bottom of the model (68 m depth), so that the water table will be at approximately 64 m depth. Initial water saturation does not affect the eventual steady state and was chosen as an arbitrary 60%. Although temperature remains constant during the simulation, its value matters as it determines water density and viscosity. Temperature boundary conditions are a mean land surface temperature of 12.8 °C, and a temperature of 17.26 °C at 68 m depth, which is (linearly) extrapolated from the value of 17 °C at 64 m depth given by Piepho (1999). For the Richards' equation approximation we use an average temperature of 15 °C for the 68 m thick domain modeled.

D.7.1.4 Results

D.7.1.4.1 Modeling and Thermal Regime. Simulation results include cross-sections of temperatures, water saturations, and fluid salinities at different times, as well as time series of various parameters at specified locations (Figure D.7.1.3). In this space it is possible to give only a brief summary of the main phenomena observed in the simulations.

Figure D.7.1.3. Locations for Monitoring Temporal Changes.

Note: (1) 30 cm below tank, 0.5 m from centerline; (2) 16.5 cm above tank, 0.5 m from centerline; (3) 4.1 depth, 29 cm from sidewall; (4) 30 cm below tank, 29 cm from sidewall.

The highly elevated temperatures in the early period, up to 1967, give rise to boiling near the tank and partial formation dryout. Formation temperatures near the tank rise to above 120 °C, and an extensive zone with temperatures near the ambient boiling temperature of 100 °C develops (see Figure D.7.1.4). This is a “heat pipe” region in which very efficient heat transport takes place by means of vapor-liquid counterflow (Eastman 1968; Doughty and Pruess 1988). The vapor generated near the tank is driven away from the heat source by pressure gradients, and subsequently condenses in cooler regions, releasing its latent heat. Water saturations near the tank are reduced, establishing a capillary pressure gradient that draws liquid water back toward the tank. This vapor-liquid counterflow system rapidly distributes the heat released from the tank over a much greater formation volume than could be accessed by heat conduction alone.

Figure D.7.1.4. Time Dependence of Temperatures at Selected Locations.

The vapor-liquid counterflow system gives rise to persistent solute transport towards the heat source, which causes solutes to become highly concentrated and even precipitate in the boiling region. Figure D.7.1.5 shows contour diagrams of the aqueous phase mass fraction of infiltrated fluid at three different times. The inventory of infiltrated fluid seems rather small in 1965.91, which is explained by noting that a large fraction of infiltrated solute tracer actually precipitates in the hot region near the tank, reducing the amount available in the aqueous phase. At time 1965.91 precipitated salt amounts to 55.3% of all NaCl that was infiltrated at the land surface. This amount of precipitation is very large, especially when considering that the infiltrating fluid is quite dilute (0.1 wt% NaCl), and highlights the remarkable capacity of the heat pipe system to concentrate solutes near the heat source. As temperatures decline the region near the tank is rewetted, both from capillary-driven liquid flow and from vapor condensation. By the end of 1974 all previously precipitated tracer is redissolved.

Figure D.7.1.5. Distribution of an Environmental Tracer Infiltrating at the Land Surface at Different Times.

The solute tracer in the infiltrating water was arbitrarily modeled as NaCl, but it can represent any conservative, non-sorbing solute. Tracer breakthrough curves at different horizons are given for the thermal and isothermal cases in Figure D.7.1.6 on a log scale. These curves were obtained by summing all tracer fluxes that cross a horizon at a certain depth, then dividing this by the total liquid flux across that same horizon, and normalizing with respect to tracer concentration in infiltrated fluid. It is seen that early arrivals of tracer are somewhat enhanced from the tank heat, but thermal effects on aggregated tracer migration are generally modest, except at the 16 m horizon right beneath the tank.

Figure D.7.1.6. Tracer Breakthrough Curves at Different Depths.

Note: Symbols are for the isothermal reference case, while lines are for the base case with tank heat

Diffusive vapor fluxes are highest near the tank, and decrease rapidly due to condensation as the land surface is approached. During high-temperature periods vapor diffusion at 0.5 m depth amounts to approximately 10% of net infiltration, while at the land surface itself the effect is less than 4% of net infiltration.

In Figure D.7.1.7 we compare simulated temperatures with appropriately corrected measurements in 41-09-39 borehole, which is a vertical hole centrally located between tanks SX-108, SX-109, SX-111, and SX-112. There is fair overall agreement between the profiles, with some significant discrepancies. It appears that tank temperatures used in the simulation may have been unrealistically high for some period of time prior to the year 2000. The elevated temperatures observed in 41-09-39 borehole below 20 m depth may be attributed to local heating from radioactive decay in fluid leaked from the tanks. This effect will be explored in future simulations and may help to better constrain the magnitude of the leak.

Figure D.7.1.7. Comparison Between Simulated Temperatures and Observations in Hole 41-09-39.

Note: The curve labeled "Simulation" corresponds to a distance of 16 m from the center of tank SX-108 at the beginning of Year 2000.

D.7.1.4.2 Tank Leak Simulations. Separate simulations were performed to investigate the behavior of a tank leak. Reliable information on location, timing, and magnitude of leaks is not available. For tank SX-108 it has been estimated that a leak occurred in the 1966 to 1968 time frame during which approximately 50,000 gallons ($= 189.27 \text{ m}^3$) of fluid were discharged into the unsaturated zone (T. Jones private communication 2000). We assume here that the leak occurred over a one-year period during 1966, so that average volumetric leak rate is $5.998 \times 10^{-6} \text{ m}^3/\text{s}$. The leaked fluid had high ionic strength and correspondingly large density. The predominant solute in the tank fluid is NaNO_3 ; however, the leak was modeled here as involving a solution of 10 wt% NaCl. This was done because a fluid property description for NaCl solutions was readily available for the temperature conditions of interest (Battistelli et al. 1997). A fluid property package for aqueous solutions of NaNO_3 is being developed as part of this research, but experimental data for this system appear to be limited to temperatures below 55°C (Isono 1984; Mahiuddin and Ismail 1996; Apelblat and Korin 1998). While not quantitatively accurate, substitution of NaCl is expected to provide a reasonably approximate outlook on system behavior. Another limitation arises from the radial symmetry of our current model, which forces tank leaks to be radially symmetric also.

Our simulation includes most but not all effects of salinity on thermodynamic and transport properties of the leaked fluid. Specifically, we include salinity effects on density, viscosity, enthalpy, and vapor pressure of the aqueous phase. Vapor pressure lowering from salinity will induce vapor diffusion towards more saline regions, where subsequent vapor condensation will cause water saturation to increase. Fluid salinity is known to affect surface tension; for example, a saturated NaCl solution at $T = 20^\circ\text{C}$ has approximately 10% larger surface tension than pure water (Adamson 1990). This effect should cause capillary pressures to be somewhat stronger in regions of higher salinity, while the decrease of surface tension with increasing temperatures would weaken capillary pressures in warmer regions. In the present simulation both these effects were neglected.

Breakthrough curves at different horizons are shown in Figure D.7.1.8. Flowing leaked fluid mass fractions at different depths were calculated as the ratio of total solute flow rate to total aqueous phase flow rate, and normalized to the solute concentration in leaked fluid (10 wt%). It is seen that inclusion of thermal effects has negligible impact on the breakthrough time of leaked fluid at 26 m depth, although the concentration of leaked fluid remains lower in the thermal case for an extended time period of approximately 20 years. At deeper horizons, thermal effects are seen to retard and weaken breakthrough of leaked fluids. A comparison case that neglects all salinity effects except solubility constraints produces very similar breakthrough curves, although there are considerable differences in details of thermohydrologic behavior. For example, at $t = 1973.66$ the simulation with simplified salinity effects predicts almost twice as much solid precipitate in the inner portion of the leakage plume beneath the center of the tank. It is expected that solute transport behavior may depend strongly on the location of the leak, being very different in the infiltration shadow beneath the center of the tank than in the region of enhanced seepage fluxes around the tank perimeter.

Figure D.7.1.8. Breakthrough Curves of Leaked Fluid Released Beneath Tank Center at Different Horizons.

Note: Symbols are for the isothermal reference case, while lines are for the base case with tank heat.

There is much evidence from field and laboratory studies that permeability in sedimentary formations tends to be anisotropic. Depending on moisture tension conditions, permeability in the horizontal direction may exceed vertical permeability by factors of from 3 to 10 or more. The physical condition that causes this anisotropy is the predominantly horizontal layering of sediments, where horizontal and vertical flow proceed via “conductors in parallel” and “conductors in series,” respectively. We have made an initial assessment of moisture tension-dependent anisotropy, using a novel two-layer (fine-coarse) model to resolve sub-grid scale heterogeneity. For the isothermal reference case, Figure D.7.1.9 compares pre-emplacement saturation distributions for static anisotropy with those for weak and strong “dynamic” (moisture tension-dependent) anisotropy. Breakthrough curves at different horizons are shown in Figure D.7.1.10. Breakthrough is seen to generally occur more slowly in the anisotropic case, as expected, but more complex behavior is noted in details.

**Figure D.7.1.9. Steady-State Water Saturation Profiles for 1 cm/yr Net Infiltration.
Two Cases with Dynamic Anisotropy are Shown.**

Note: The line labeled "Static" corresponds to the reference case with a tension-independent anisotropy factor of 3 (2 for backfill).

Figure D.7.1.10. Breakthrough Curves of Leaked Fluid Released Beneath the Tank Center on Logarithmic (top) and Linear Scale (bottom).

Note: Symbols are for the isothermal reference case, and lines are for the case of "Strong" anisotropy. The data at 26 m depth refer to the left axis, the 45 m data to the right.

D.7.1.5 Conclusions and Implications

Moisture distribution, fluid flow, and solute transport beneath tank SX-108 were strongly affected by tank heat, salinity of leaked fluids, and multiphase processes that include boiling and condensation, partitioning of species among phases, and multiphase flow and transport. A sound assessment of solute behavior must include all of the important physical and chemical processes, and must employ realistic parameters for the different flow and transport processes and for hydrogeologic conditions. In this report we have presented preliminary simulations that have focused primarily on thermo-hydrologic effects, and have adopted a simplified layer-cake stratigraphy. Our simulations show that during the period of above-boiling tank temperatures, the fluid flow and heat transfer regime in the region surrounding the tank is dominated by vapor-liquid counterflow effects. Vapor-liquid counterflow provides a very efficient heat transfer mechanism known as "heat pipe," that rapidly dissipates tank heat over a large volume. The heat pipe system is also very efficient at concentrating dissolved solutes near the heat source, where precipitation of solids occurs as aqueous concentrations in boiling regions exceed solubility limits even for solutes whose initial concentrations in formation waters are small.

Exploratory calculations were performed to study the behavior of tank leaks, and to investigate effects of layering anisotropy. Thermal effects were found to generally retard and reduce downward migration of solutes released from beneath the tank. However, only leaks beneath the

center of the tank have been investigated so far. The observed trends may be specific to leak location, and different behavior may be expected for leaks near the tank perimeter. Some of the simulations presented here include a comprehensive treatment of salinity effects on density, viscosity, enthalpy, and vapor pressure of the aqueous phase. These effects were found to partially compensate one another, so that in some cases approximations that neglect most salinity effects may be justified. Salinity effects have so far been modeled by using NaCl as dissolved solid. This was done because for aqueous NaCl the required thermophysical data were available over the entire temperature range of interest. Work is ongoing to develop a thermophysical properties package for NaNO_3 solutions, which would provide a better representation of leaked fluids.

A new model was developed to investigate effects of sub-grid scale anisotropy on unsaturated flow and transport in the layered sediments at Hanford. Formation anisotropy was found to be capable of considerably slowing the downward migration of solutes.

Among the issues that remain to be addressed in future work, perhaps the most important ones are (1) comparison with field data on temperatures, moisture content, and solute distributions, and (2) more detailed three-dimensional representation of hydrogeologic conditions at tank SX-108. Additional topics for future work include parameter sensitivities (absolute permeability, characteristic curves, small-scale layering, dependence of thermal conductivity on moisture status, dependence of capillary pressure strength on temperature and salinity), thermal effects of leaked fluid, interference between tanks, and couplings between thermal, hydrologic, and chemical processes. We also plan to explore multi-region effects on solute transport, and to investigate future solute transport behavior under “no action” conditions, as well as for scenarios that involve placing infiltration covers over the tanks, and fluid losses during possible future sluicing operations to remove tank wastes.

D.7.1.6 Acknowledgement

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D.7.2 NONISOTHERMAL MULTIPHASE FLUID FLOW AND TRANSPORT: MULTITANK MODELING IN THE SX TANK FARM

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D.7.2.1 Introduction

The objective of ~~this~~ numerical investigation was to contribute to the understanding of the thermal and multifluid environment surrounding the single-shell tanks within the WMA S-SX on the Hanford Site, near Richland, Washington. In particular, this investigation considered the thermal and hydrogeologic environment surrounding the westing row of tanks in the center of the WMA S-SX (i.e., tanks SX-107, SX-108 and SX-109) and its effects on the transport of a conservative radionuclide to the WMA border. This row of tanks was selected because tanks SX-108 and SX-109 had histories of high heat loads and elevated temperatures, and tank SX-108 was known to have leaked radionuclides and other contaminants into the subsurface. This study used numerical simulation to investigate the coupled processes of multifluid flow, heat transfer, and solute transport in a heterogeneous geologic environment surrounding the subject row of single-shell tanks. Ancillary investigations of solute transport from the WMA S-SX (White et al. 2001) demonstrated that two-dimensional cross-sectional simulations could be used without introducing significant errors to model the three-dimensional subsurface environment surrounding the single-shell tanks.

Accurate hydrologic modeling of the WMA S-SX requires a comprehensive description of the site hydrogeology, tank thermal and leak histories, hydrologic conditions at the ground surface and water table, and their variability. The hydrogeologic description of the WMA S-SX implemented in this investigation was a modified version of the data package (Khaleel et al. 2000) provided for a complementary study of solute transport under isothermal conditions.

All simulations reported herein were executed with the STOMP simulator (White and Oostrom 2000 a, b), using the Water Operational Mode for isothermal simulations and the Water-Air-Energy Operational Mode for the nonisothermal simulations. All simulations considered the transport of the solute ⁹⁹Tc from known distributions in the year 2000, ~~as~~ specified in the modeling data package (MDP) (Khaleel et al. 2000). Grid resolutions for all simulations were 0.5334 m (1.75 ft) horizontally and 0.4572 m (1.5 ft) vertically. The isothermal simulations use the assumption of a passive gas phase, where the gas phase is assumed to have a constant pressure of 101325.0 Pa (1 atm). Transport of phase components (i.e., water and air) and solutes are neglected under the passive gas assumption. Gas entrapment by the wetting phase (i.e., aqueous phase) was neglected for both the isothermal and nonisothermal simulations. The nonisothermal simulations use the assumption of an active gas phase; however, ⁹⁹Tc transport was only considered in the aqueous phase. The numerical modeling of this investigation does not consider chemical interactions with the porous media, nor does it consider heat generated through chemical reaction or radiological decay. The transported solute is assumed to be “infinitely dilute” with respect to altering the properties of the transporting

medium. For example the aqueous-phase density was assumed to be dependent on temperature and pressure, but independent of the dissolved-solute concentration. A more comprehensive analysis would consider the heat contribution from radioactive decay, chemical interactions with the porous media, including dissolution and precipitation, which may significantly alter local hydrologic properties and fluid property dependence on solute concentration. The modeling analysis described in this report should be considered preliminary to a more comprehensive representation of the hydrologic flow and transport processes which occurred and continue to proceed in the subsurface environment surrounding the single-shell tanks at the Hanford Site WMAs.

D.7.2.2 Modeling Procedures

The simulations executed for this investigation followed the specifications of the Base Case scenario for the cross-section through tanks SX-107, SX-108, and SX-109 of the modeling data package (Khaleel et al. 2000). This scenario involved simulating flow and transport considering natural infiltration only, with no water line leaks, no tank leaks, no interim surface barrier, a closure barrier by the year 2040, and a uniform distribution of initial solute inventory. For the isothermal simulation aqueous flow was considered and for the nonisothermal simulation, coupled aqueous and gas flow and heat transfer was considered. For both simulations only the transport of the solute ^{99}Tc was investigated. Isothermal simulation results for all case scenarios and solute species described in the MDP (Khaleel et al. 2000) are reported separately (White et al. 2001).

The geology of the subject cross-section was a modified version of the WMA S-SX Cross-Section D-D' reported by Price and Fecht (1976) as specified in the MDP (Khaleel et al. 2000). The Khaleel modifications principally involved combining like soil types, yielding five different strata: (1) backfill, (2) sand, (3) gravelly sandsandy gravel, (4) Plio-Pleistocene (including caliche), and (5) sandy gravel. Because the dominant geologic feature at the Hanford site is a layered structure of depositional sediments, the soil units are commonly referred to as strata. The geology for the subject cross section is generally layered (see Figure D.7.2.1), except for the sloping layer of material identified as gravelly sandsandy gravel that extends from just underneath tank SX-107, sloping downward toward the west beneath tanks SX-108 and SX-109. The other anomaly to the layered system is the trench of backfill material near the ground surface, which surrounds the tanks. Not included in this simplified geology is the 2 m of gravel and coarse sand placed on top of the tanks, the layer of compacted material placed beneath the tanks, pinched-off sublayers identified in the original geologic interpretations, and known clastic dikes.

Figure D.7.2.1. Geology for Cross-Section Through Tanks SX-107, SX-108, SX-109.

Hydrogeologic properties include functions and/or parameters that define a soil's porosity, intrinsic permeability, tortuosity, bulk density, thermal conductivity, soil-moisture retention characteristics, and phase relative permeability. Hydrogeologic properties for the isothermal and nonisothermal simulations were obtained from the MDP (Khaleel et al. 2000), except for the aqueous- and gas-phase relative permeability functions, which were changed from the Mualem porosity distribution function (Mualem 1976) with Polmann anisotropy (Polmann 1990) to the Corey function (Corey 1954). The Corey aqueous- and gas-phase relative permeability functions are defined according to Equations D.7.2.1 and D.7.2.2, respectively

$$k_{rl} = (\bar{s}_l)^4 \quad (\text{D.7.2.1})$$

$$k_{rg} = (1 - \bar{s}_l)^2 (1 - (\bar{s}_l)^2) \quad (\text{D.7.2.2})$$

where k_{rl} is the aqueous-phase relative permeability, k_{rg} is the gas-phase relative permeability, and $\bar{s}_l$ is the effective aqueous saturation. The hydrogeologic properties for each of the five defined soil types are summarized in Table D.7.2.1.

Table D.7.2.1. Hydrogeologic Properties.

Soil/Property	Backfill	Sand	Gravelly Sand	Plio-Pleistocene	Sandy Gravel
Porosity	0.138	0.382	0.213	0.435	0.138
Residual saturation	0.0725	0.116	0.0151	0.153	0.0725
Saturation function	van Genuchten [1980]	van Genuchten [1980]	van Genuchten [1980]	van Genuchten [1980]	van Genuchten [1980]
van Genuchten α , 1/cm	0.021	0.0117	0.0141	0.0085	0.021
van Genuchten	1.3740	1.6162	1.3730	1.8512	1.3740
Vertical hydraulic conductivity, cm/s	5.60×10^{-4}	9.88×10^{-5}	2.62×10^{-4}	2.40×10^{-4}	5.60×10^{-4}
Horizontal hydraulic conductivity, cm/s	5.60×10^{-3}	9.88×10^{-4}	2.62×10^{-3}	2.40×10^{-3}	5.60×10^{-3}
Particle density, kg/m ³	2650.	2650.	2650.	2650.	2650.
Dry thermal conductivity, W/m K	0.25	0.25	0.25	0.25	0.25
Wet thermal conductivity, W/m K	2.0	2.0	2.0	2.0	2.0
Thermal conductivity model	Somerton et al. [1973]	Somerton et al. [1973]	Somerton et al. [1973]	Somerton et al. [1973]	Somerton et al. [1973]
Particle specific heat, J/kg K	750.	750.	750.	750.	750.
Longitudinal dispersivity, cm	150	180	100	80	180
Transverse dispersivity, cm	15	15	10	5	15
Tortuosity model	Millington and Quirk [1961]	Millington and Quirk [1961]	Millington and Quirk [1961]	Millington and Quirk [1961]	Millington and Quirk [1961]

Boundary conditions for the isothermal and nonisothermal simulations ignored the temporal fluctuations in meteoric recharge, atmospheric relative humidity, ground-surface temperature, water table elevation and cross-flow gradient, and aquifer temperature. Changes in meteoric recharge were considered for changes in surface barriers. Heat generation in tanks SX-108 and SX-109 were modeled by specifying tank surface temperatures as a function of time.

The boiling temperature of the subject tanks has been estimated as 112°C^(a), whereas sludge temperatures at the bottom of the tank have been measured in excess of 140°C. With these guidelines, tank surface temperatures assignments were binned into two categories: (1) tank vertical walls and top and (2) tank bottom. Tank vertical wall and top surfaces were assigned a

(a) Tom Jones, U.S. Department of Energy, Richland, Washington (private communications).

temperature equal to the minimum of 112 °C and the reported tank temperature history (Agnew and Corbin 1998). Tank bottom surfaces were assigned a temperature equal to those reported for the tank. S and SX tank farms were covered with gravel and coarse sands to prevent vegetative growth and provide radiation shielding. Bare gravel, however, significantly reduces the amount of meteoric moisture that is returned to the atmosphere through evaporation and plant transpiration. Drainage from bare sands has been estimated at 70 mm/yr under Hanford climatic conditions (Ward et al. 1997). No direct measurements have been made for tank-farm gravels; however, earlier studies have suggested recharge rates of 130 mm/yr for gravel-covered waste sites (Gee et al. 1992). Meteoric recharge for these investigations was assumed to follow the values shown in Table D.7.2.2. The ground-surface temperature and relative humidity were held at 12.8 °C and 30%. The 30% relative humidity condition was used to reflect Hanford climatic conditions. The bottom of the computational domain (71.32 m-bgs) was modeled as a no flux boundary for aqueous- and gas-phase flow with a held temperature of 17.26 °C. The lowest 5.944 m on the vertical sides of the domain were modeled as constant aqueous pressure conditions, where a hydrostatic variation in pressure was used vertically. These boundary conditions created a water table at 65.46 m-bgs on the left side and 65.68 m-bgs on the right side resulting in a cross-flow hydraulic gradient of 1.3×10^{-3} . Temperatures on these sections of vertical boundaries were held at 17.26 °C.

Table D.7.2.2. Recharge Boundary Condition.

Condition	Recharge (mm/yr)
No Barrier [1955.82-2010]	100.
Interim Barrier [2010-2040]	0.5
Closure Barrier 12040-25401	0.1
Degraded Barrier [2540-3000]	3.5

Time dependent boundary conditions for the tank SX-108 and SX-109 surfaces are shown in Figure D.7.2.2. The surfaces of tank SX-107 were treated as impermeable to aqueous and gas flow and adiabatic to heat transfer. The adiabatic thermal boundary condition ignores material inside the tank and heat transfer across the tank surfaces. This approach yields unlikely temperature contours around tank SX-107, which could be corrected if additional information about the temperatures inside the tank or content histories were incorporated into the simulation.

Figure D.7.2.2. Temperature Histories for Tanks SX-108 and SX-109.

D.7.2.3 Results

D.7.2.3.1 Historical Thermal Regime. The thermal response of the hydrogeologic environmental surrounding tanks SX-107, SX-108 and SX-109, as predicted by the numerical simulation, is shown as a series of color-scaled contour plots for specified times in Figures D.7.2.3 through D.7.2.13. The hydrologic response is shown as a series of color-scaled contour plots of saturation differential in Figures D.7.2.14 through D.7.2.24. For these figures saturation differential refers to the change in saturation from the initial steady-flow condition. The thermal response begins as a linear gradient in temperature from the water table at 17.2 °C to the ground surface at 12.8 °C. From this point, starting at 1955.82, the surface temperatures of tanks SX-108 and SX-109 rise above ambient conditions as they are used for storage of heat-generating liquid waste, where the surface temperatures followed the histories shown in Figure D.7.2.5. After 0.1 years, the soil immediately surrounding the heated tanks begins to increase in temperature (Figure D.7.2.3) reaching a maximum temperature of 103.3 °C. After 0.5 years, the temperature beneath the heated tanks increases to 106.5 °C (Figure D.7.2.4) and dryout of the soils at this point begins to occur (Figure D.7.2.15). The maximum change in saturation is a decrease of 0.24. Water displacement occurs by evaporation, migration and recondensation of water vapor through the gas phase. Because of its higher permeability, water vapor transport away from the heated tanks generally occurs along the sloped gravelly sand layer, yielding higher water saturations in this strata. This progression of increasing temperature and soil dryout continues to 2 years (Figures D.7.2.5 to D.7.2.8 and D.7.2.16 to D.7.2.17).

Figure D.7.2.3. Temperature Profile at 1955.92 (+0.1 yr).

Figure D.7.2.4. Temperature Profile at 1956.32 (+0.5 yr).

Figure D.7.2.5. Temperature Profile at 1956.82 (+1 yr).

Figure D.7.2.6. Temperature Profile at 1957.82 (+2 yr).

Figure D.7.2.7. Temperature Profile at 1960.82 (+5 yr).

Figure D.7.2.8. Temperature Profile at 1965.82 (+10 yr).

Figure D.7.2.9. Temperature Profile at 1970.82 (+15 yr).

Figure D.7.2.10. Temperature Profile at 1975.82 (+20 yr).

Figure D.7.2.11. Temperature Profile at 1980.82 (+25 yr).

Figure D.7.2.12. Temperature Profile at 1990.82 (+35 yr).

Figure D.7.2.13. Temperature Profile at 2000 (+45 yr).

Figure D.7.2.14. Saturation Differential Profile at 1955.92 (+0.1 yr).

Figure D.7.2.15. Saturation Differential Profile at 1956.32 (+0.5 yr). **Figure D.7.2.16. Saturation Differential Profile at 1956.82 (+1.0 yr).**

Figure D.7.2.17. Saturation Differential Profile at 1957.82 (+2 yr). **Figure D.7.2.18. Saturation Differential Profile at 1960.82 (+5 yr).**

Figure D.7.2.19. Saturation Differential Profile at 1965.82 (+10 yr).

Figure D.7.2.20. Saturation Differential Profile at 1970.82 (+15 yr).

Figure D.7.2.21. Saturation Differential Profile at 1975.82 (+20 yr). **Figure D.7.2.22. Saturation Differential Profile at 1980.82 (+25 yr).**

Figure D.7.2.23. Saturation Differential Profile at 1990.82 (+35 yr).

Figure D.7.2.24. Saturation Differential Profile at 2000 (+44.2 yr).

Between mid 1957 and 1961 the surface temperature of tank SX-109 drops linearly from 121 to 60 °C. This temperature drop results in a shift of the thermal environment and soil moisture (Figures D.7.2.6 to D.7.2.7 and D.7.2.17 to D.7.2.18). Most notable is the resaturation of the zone immediately beneath tank SX-109, which occurs via transport of liquid water back to the region under the capillary gradient created during the dryout period. Between 1961 and 1963 the surface temperature of tank SX-109 increases to 140.6 °C, whereas tank SX-108 falls to 104.4 °C. The temperature and saturation differential profiles (Figures D.7.2.8 and D.7.2.19,

respectively) in late 1965 show the rapid dryout beneath tank SX-109 with migration of water toward the west. Resaturation occurs beneath tank SX-108 even though the tank surface temperature remains above the atmospheric boiling point (100 °C). After 1963, the surface temperature of tank SX-109 gradually decreases over a period of 10 years to a level that fluctuates between 60 and 70 °C. Tank SX-108 remains at elevated temperatures until 1967 when it drops sharply to 90 °C and then sharply again to below 60 °C near the end of 1973. In the period between late 1962 and late 1968, the sustained tank surface temperatures above 100 °C create a large dryout region and constant temperature region beneath the tanks (Figures D.7.2.19 to D.7.2.20 and D.7.2.8 to D.7.2.9, respectively). In late 1965, the 100 °C temperature region extends to a point roughly 75 ft below the bottom of the tanks. Saturation decreases during this period are greatest within the sloping gravely-sand strata and saturation increases from displaced moisture can be seen deep in the vadose zone.

The 100 °C temperature region that forms beneath and between the tanks comprises three zones of heat transport. In the zone nearest the tank surfaces, soil temperatures rise toward the tanks from 100 °C to the time-dependent tank surface temperature. Soil moisture in this region exists below the residual saturation and strong capillary pressures produce a reduction in the water vapor pressure. Heat transfer in this zone occurs primarily by conduction through the dried-out soil. The second zone is the constant temperature zone, which occurs beyond the dry-conduction zone nearest the tanks. Heat transfer in this region is dominated by counter-current flow of water vapor away from the tanks and liquid water toward the tanks, commonly referred to as the "heat-pipe" effect. Unlike conventional heat pipes, however, heat-pipe type flow regions in geologic media are dynamic, expanding and contracting according to the heat flux, moisture-retention characteristics of the soils, thermal conductivity of the soils, driving temperatures, and hydrologic conditions. A small transition region occurs between the dry-conduction and constant-temperature zones, which contains both conduction and heat-pipe modes of heat transfer. Evaporation of the counter-flow liquid water occurs primarily in this small region. The third heat-transfer zone occurs at the low-temperature perimeter of the constant-temperature zone. Heat transfer in this zone primarily is by conduction through soils of elevated saturation. A small transition region also occurs between the constant-temperature zone and this wet-conduction zone. Condensation of the counter-flow water vapor occurs in this small region.

In the time period between 1968 and 1978 the tank surface temperatures decay to levels between 60 and 70 °C, and after 1978 tank surface temperatures were maintained at 71.1 and 68.9 °C, respectively, for tanks SX-108 and SX-109. During this period, the thermal field and hydrologic conditions beneath the tanks transition from being dominated by heat-pipe type heat transport and counter-current flow to combined conduction/heat-pipe heat transport with weaker counter-current flow (Figures D.7.2.11 through D.7.2.13 and D.7.2.22 through D.7.2.24). With steady tank-surface temperatures and surface recharge the thermal and hydrologic fields approach steady-flow conditions that differ from the hydrologic field under the isothermal assumption. The tank-surface temperatures of 70 °C produce drier soils that extend deep in the vadose zone. Under steady-flow conditions the thermal and hydrologic fields are controlled by the rate of surface recharge, temperature of the meteoric water, tank-surface temperature, and the unconfined aquifer temperature.

The ground surface was assumed to be maintained at 12.7°C and 30% relative humidity. Under these conditions steep temperature gradients form between the tank domes and ground surface. Water vapor migration in this region is primarily by diffusion through the gas phase with the driving force being controlled by gradients in water-vapor partial pressure. Steep gradients in water-vapor partial pressure above the tank domes, causes water vapor to diffuse vertically toward the ground surface, but the constant temperature assumption of 12.7°C for the ground surface creates a 100°C contour within the soil; therefore, a water-vapor-condensation zone. Because of this condensation the amount of water vapor leaving the ground surface is relatively small (less than 2%) compared with the meteoric recharge as shown in Figure D.7.2.25. More realistic boundary conditions at the ground surface would consider allowing the ground-surface temperature to be determined through a convective-radiative heat transfer coefficient to the above-ground air temperature. A more comprehensive analysis at the ground surface, considering time variation in temperature, relative humidity, wind speed, solar insolation, ground-surface albedo, for example, was not warranted because of the constant meteoric recharge assumption.

Figure D.7.2.25. Water-Vapor Flux at the Ground Surface, % of Meteoric Recharge.

D.7.2.3.2 Comparisons with Field Measurements. Actual thermal and hydrologic conditions in the subsurface surrounding and beneath the WMA S-SX tanks are a function of environmental factors at the ground surface and unconfined aquifer, radiological heat sources of liquids stored in the tanks, past leaks from storage tanks and water lines and operational procedures for the tanks (e.g., ventilation rates, cooling techniques). It is not presumed that the simulations of this investigation will yield accurate representations of the thermal or hydrologic fields in the subsurface at the WMA S-SX. The conceptual models, on which they were founded, lack historical information related to the natural environment and engineered systems and only considered a two-dimensional cross-section through a three-dimensional domain. Two images, however, are provided that compare simulation results for the year 2000 in terms of moisture content and temperature against field measurements taken from monitoring wells within the WMA S-SX. Color-scaled contours of modeled and down-borehole measurements of soil

moisture content are shown for comparison at the year 2000 (Figure D.7.2.26). Field measurements of soil moisture were made with neutron probes, which are affected by gamma radiation. Red regions within the boreholes are generally an indication of ^{137}Cs contamination or other gamma emitting radionuclide sources. In general the well measurements show greater variability in soil moisture than the simulated results and the moisture content in the backfill material is generally higher than predicted by the simulation. Both the simulated and field measured results show lower moisture contents in the sloping gravely-sand strata and there is good correspondence between simulated and measured moisture contents for those regions beneath the tanks.

Figure D.7.2.26. Color-Scaled Contours and Well Logs of Moisture Content (2000).

In 2000, temperatures were measured along the length of two boreholes near tanks SX-109 and SX-108: 41-09-39 borehole and the SX-108 slant borehole, respectively. These boreholes are not in the plane of the modeling domain and as such, they are not directly comparable to the simulated temperature contours. However, the projection of these two borehole temperatures onto the modeling results (Figure D.7.2.27) does show a general agreement with the magnitude of predicted temperatures, especially for 41-09-39 borehole. The general discrepancy is that the peak temperatures are observed about 30 feet below the bottom of the tank rather than the predicted peak at the tank bottom. The depth of the observed peak temperature would seem to indicate that this is a residual heat signature from a historic leak of high temperature tank fluid.

Figure D.7.2.27. Color-Scaled Contours and Well Logs of Temperature (2000).

D.7.2.3.3 Solute Transport. Solutes migration through geologic media is governed by the mechanisms of advection, diffusion and hydraulic dispersion, subject to phase partitioning and sorption to the media. The simulations of solute transport in this investigation considered the migration of ^{99}Tc as a nonreactive (i.e., unretarded) species, soluble only in the aqueous phase (i.e., no partitioning into the gas phase). Initial distributions of ^{99}Tc inventory were derived from field measurements and were assumed to represent the distribution at the year 2000. Therefore, simulations of ^{99}Tc migration in this investigation were restricted to the period following the year 2000 and, thus, do not consider solute migration during the known leak events or during the period of heat-pipe conditions in the thermal and hydrologic fields.

The progression of ^{99}Tc migration from 2001 to 2100 is shown for the nonisothermal and isothermal simulation in the color-scaled contours of dissolved ^{99}Tc concentration in Figures D.7.2.28 through D.7.2.38. To enhance the visualization of the plume migration logarithmic color-scaling was used to contour the dissolved concentrations in this series of images. The distribution of dissolved ^{99}Tc in 2000.01 (Figure D.7.2.28) is nearly identical to the initial distribution assigned in 2000 according to the modeling data package (Khaleel et al. 2000). By 2001 (Figure D.7.2.29), however, significant dispersion of the plume has occurred and there is evidence of preferential migration along the sloping gravelly-sand strata. Because the ^{99}Tc inventory was initially distributed primarily below this strata, its effect on the lateral migration of ^{99}Tc is limited. The dissolved ^{99}Tc plume migrates rapidly over the first 40 years (Figures D.7.2.30 through D.7.2.33) toward the unconfined aquifer, where it dilutes and is transported laterally toward the WMA S-SX eastern boundary. At 2040 a closure barrier becomes effective, reducing the surface recharge and consequentially slowing the downward migration of ^{99}Tc (Figures D.7.2.33 through D.7.2.38). A plot of ^{99}Tc concentrations at the

WMA S-SX boundary versus time is shown in Figure D.7.2.39 for both the isothermal and nonisothermal simulations. Peak concentrations of ^{99}Tc at the WMA S-SX boundary were predicted to be 1.575×10^6 pCi/L at year 2040.3 for the isothermal simulation.

Figure D.7.2.28. Dissolved ^{99}Tc Concentration Profile at 2000.01 (+0.01 yr).

Figure D.7.2.29. Dissolved ^{99}Tc Concentration Profiles at 2001 (+1 yr)
(Nonisothermal: Color-Scaled, Isothermal: Black Contour Lines).

Figure D.7.2.30. Dissolved ^{99}Tc Concentration Profile at 2010 (+10 yr)
 (Nonisothermal: Color-Scaled, Isothermal: Black Contour Lines).

Figure D.7.2.31. Dissolved ^{99}Tc Concentration Profile at 2020 (+20 yr)
 (Nonisothermal: Color-Scaled, Isothermal: Black Contour Lines).

Figure D.7.2.32. Dissolved ^{99}Tc Concentration Profile at 2030 (+30 yr)
 (Nonisothermal: Color-Scaled, Isothermal: Black Contour Lines).

Figure D.7.2.33. Dissolved ^{99}Tc Concentration Profile at 2040 (+40 yr)
 (Nonisothermal: Color-Scaled, Isothermal: Black Contour Lines).

Figure D.7.2.34. Dissolved ^{99}Tc Concentration Profile at 2050 (+50 yr)
 (Nonisothermal: Color-Scaled, Isothermal: Black Contour Lines).

Figure D.7.2.35. Dissolved ^{99}Tc Concentration Profile at 2060 (+60 yr)
 (Nonisothermal: Color-Scaled, Isothermal: Black Contour Lines).

Figure D.7.2.36. Dissolved ^{99}Tc Concentration Profile at 2070 (+70 yr)
 (Nonisothermal: Color-Scaled, Isothermal: Black Contour Lines).

Figure D.7.2.37. Dissolved ^{99}Tc Concentration Profile at 2080 (+80 yr)
 (Nonisothermal: Color-Scaled, Isothermal: Black Contour Lines).

**Figure D.7.2.38. Dissolved ^{99}Tc Concentration Profile at 2100 (+100 yr)
(Nonisothermal: Color-Scaled, Isothermal: Black Contour Lines).**

Figure D.7.2.39. Dissolved ^{99}Tc Concentration at the WMA S-SX Boundary.

D.7.2.4 Conclusions and Implications

The fundamental implication of this investigation to the future management of the WMA S-SX is that the thermal and hydrologic environment of the subsurface is strongly coupled. Therefore, in order to understand historical behavior and predict future migration of contaminants around and beneath the WMA S-SX tanks, it is crucial to consider this coupling between the thermal and hydrologic conditions. The simulations of ^{99}Tc migration into the future under isothermal and

nonisothermal conditions, suggest that the current thermal conditions beneath the tanks do not significantly alter the behavior of this nonreactive contaminant. For investigations that will consider future tanks leaks from retrieval activities (e.g., sluicing, salt-cake dissolution) the implication of this investigation is that the coupled nature of the thermal and hydrologic environments be considered.

Radiological heat sources from previous tank leaks was not considered during these investigations. The strong heat-pipe type flow regimes that developed during the late 1960s and early 1970s beneath tanks SX-108 and SX-109 would tend to concentrate aqueous soluble radionuclides near the water evaporation zone (i.e., the transition region between the dry-conduction zone and the counter-current or constant-temperature zone). Concentration of mobile radionuclides using this mechanism could produce local radiological decay heat sources. The simulation results additionally indicate that the influence of these solute concentrating heat-pipe type flow regimes extended roughly 75 feet beneath tanks SX-108 and SX-109. The implication here is that future investigations may need to address thermal and hydrologic coupling for localized heat generation by radionuclide decay.

This investigation was principally directed at understanding the impact of thermal-hydrological coupling on the transport of mobile radionuclides to the unconfined aquifer. Though this investigation has demonstrated the importance of the coupled effect the simulation results additionally show the critical role of a surface barrier in retarding the downward migration of mobile solutes. The implication is that surface recharge strongly influences downward migration of solutes and surface barriers or other engineered technologies that reduce meteoric recharge will lower peak concentrations and delay peak arrival times of these species. This further suggests that early application of an interim surface barrier would have strong merit. Under constant ground-surface temperature and meteoric recharge conditions, the diffusive **flux** of water vapor vertically through the ground surface is less than 2% of the meteoric recharge. If the ground-surface temperature had been computed using a radiative-convective heat transfer coefficient the percent of meteoric recharge lost through the ground surface would be higher.

D.7.2.5 References

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D.7.3 ESTIMATION OF TANK SUPERNATANT LIQUID COMPOSITIONS

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D.7.3.1 Introduction

Leaks that have occurred from single-shell tanks containing high-level radioactive waste in the 200 Area of the Hanford Site contain high ionic strength fluids that can adversely affect the migration of radionuclides. It is expected that these fluids reacted strongly with the sediments beneath the tanks, very likely altering their sorptive properties. Furthermore, competitive sorption effects for the limited number of sorption sites between radionuclides and cations in the background electrolyte solution leaked from the tanks could enhance the mobility of certain radionuclides.

In order to use quantitative models to describe the movement of radionuclides, which have leaked from many of the single-shell tanks (it has been estimated that 67 out of 149 single-shell tanks have leaked), an estimate of the chemical composition of the fluid is required.

Determining the tank leak composition is a highly nontrivial task. Unfortunately, because of the highly radioactive nature of the tank inventory, and because tank inventories varied over time, direct measurements are not available. Thus, indirect approaches must be used to estimate the composition of each tank at the time it was suspected to have leaked.

Tank inventories fluctuated over time depending on their fill histories, heat load, and evaporative loss. Precipitates composed of sodium nitrate and nitrite and alumina among others are likely to have formed in the tanks. Timing of leak events have been estimated based on unaccounted volume losses using the Historical Leak Model (HLM) corroborated with reports of lateral and drywell contamination (Agnew and Corbin 1998). Tank waste inventories can be estimated as functions of time using the Hanford Defined Wastes (HDW) model developed by Agnew (1997). The HDW model takes into account blending and concentration of the wastes over time. Considerable disagreement, however, still exists over the volume of fluid that has leaked from the various tanks and its composition (Agnew and Corbin 1998; Jones et al. 2000). An exception is tank SX-115 for which relatively accurate data exists for leak timing and volume.

Once a best estimate for the tank inventory has been obtained at the time of the leak, it is still necessary to determine the composition of the tank supernate liquid, the most likely phase to have leaked from the tank. Assuming the supernate is in equilibrium with salts precipitated in the tanks, a thermodynamic model is needed to determine the equilibrium phase assemblage consistent with a given tank inventory. The high ionic strength of the supernate liquid characteristic of several of the tanks in the SX tank farm, places severe requirements on thermodynamic models that can be used for this purpose. In this contribution, the Pitzer activity coefficient algorithm as developed for the GMIN computer code (Felmy 1995) and its associated database, is implemented into the reactive transport code FLOTRAN (Lichtner 2001). Equilibration of the tank inventory is carried out using a reaction path simulation from which both the supernate composition and the stable mineral assemblage at equilibrium are determined simultaneously.

D.7.3.2 Modeling Approach

Tank waste compositions estimated using the HDW model represent a combination of contributions from both liquid and solid (saltcake) inventories. Because the liquid phase is considered to be the main fraction of the tank inventory lost during a leak event, it is necessary to obtain an estimate for the liquid composition alone. Direct use of the tank waste inventory itself would lead to an unrealistic estimate of the liquid phase composition, resulting in a solution highly supersaturated with respect to a number of minerals. The composition of the supernate liquid in the tank may be determined by calculating the equilibrium configuration of liquid and solid phases starting with the same total mass balance as the tank waste inventory.

D.7.3.2.1 Reaction Path Formulation. There are two basic approaches available for calculating the composition of the liquid fraction of the tank inventory and the solids with which it is in equilibrium. One approach is to minimize the Gibbs free energy of the system consisting of liquid and solids. This approach is independent of any particular reaction stoichiometry. It involves the free energy of each species at the temperature and pressure of interest, and mass balance and electroneutrality constraints. The result of the minimization process provides the composition of the liquid phase and the number of moles of each solid, which is present in the final equilibrium state. A gas phase may also be present.

An alternative, equivalent approach, is based on the explicit treatment of chemical reactions formulated for a particular, nonunique, reaction stoichiometry. An equilibrium constant for each chemical reaction is required along with species mass conservation relations.

The equivalent procedure to minimizing the Gibbs free energy in the reaction-based approach is to perform a reaction path, or titration, calculation in a closed system. Both of these approaches determine the equilibrium state of a closed system from some initial configuration. Because this equilibrium state is unique and independent of the path the system follows to reach equilibrium (Prigogine and Defay 1954), the two approaches must yield identical results assuming equivalent thermodynamic data in the form of free energies or equilibrium constants, and the same treatment of activity coefficient corrections.

The way in which chemical reactions are incorporated into the two models is an important distinction. In the stoichiometric reaction approach, aqueous species are partitioned into primary and secondary species. Chemical reactions are formulated for secondary species in terms of the primary species that serve as a set of basis species. The secondary species consist of ion pairs, complexes, dissociation products (such as OH^-), and related species. Minerals are treated in a similar fashion by writing reactions containing a single mineral in terms of the chosen set of primary species. Because the equilibrium configuration of a closed system is independent of the particular form of the chemical reactions used to represent the system, in the equilibrium constant approach any set of linearly independent reactions may be used (Prigogine and Defay 1954). Thus so long as a linearly independent set of reactions are provided, any of the primary species may be replaced by any of the secondary species. Only when describing kinetic behavior of the system does reaction stoichiometry play a role.

Reaction path calculations may be carried out using several different approaches. One approach is to formulate the problem in terms of a reaction progress variable and to enforce chemical

equilibrium on the system at each step along the reaction path. Another approach is to use real time as the progress variable combined with arbitrary reaction kinetics for solid phases. This latter approach is followed in this report using the computer code FLOTRAN (Lichtner 2001). FLOTRAN incorporates the Pitzer model adapted from GMIN (Felmy 1995) for activity coefficient corrections for high ionic strength fluids. In addition, a Debye-Huckel algorithm is available for more dilute solutions. The solvent species, in this case water, is included in mass balance equations, as is the deviation of the activity of water from unity. This is essential for the highly concentrated solutions that characterize some of the tank waste. Mineral reactions are treated with a transition state pseudo-kinetic rate law. Homogeneous reactions within the aqueous phase, such as ion pairing, complexing, redox reactions, and dissociation of water, are assumed to obey conditions of local chemical equilibrium. All thermodynamic data is read from a single database that must be provided by the user. The database used for the calculations in this report is derived from the EQ3/6 database, version data0.com.V8.R6. The database provides equilibrium constants over a range of temperatures from 0 to 300 °C with pressure at 1 bar, or taken along the saturation curve of pure water for temperatures above 100 °C. Additional databases provided by GMIN are required for the various Pitzer parameters when using the Pitzer activity coefficient algorithm. It should be noted, however, that the GMIN database does not extend below 25 °C and is limited to temperatures less than or equal to 100 °C for many species.

The reaction path formulation has a number of advantages over the free energy minimization approach. In the first place, the reaction path method enables a true kinetic formulation of reaction rates for a system in partial chemical equilibrium. Secondly, many of the objections that have been raised against the stoichiometric formulation (e.g., Harvie et al. 1987) disappear when this approach is combined with a real time, pseudo-kinetic, description of mineral reactions. It then becomes an easy and automatic process to determine the stable equilibrium mineral assemblage. Because it is not possible to know in advance which minerals are present at equilibrium, a sufficient number of possible mineral reactions must be included in the reaction path calculation to resolve the final equilibrium state of the system. Some of these minerals may precipitate during the early stages of the reaction path calculation, but completely dissolve at later times and hence not appear in the final equilibrium state. This approach enables the equilibrium mineral assemblage to be determined "automatically" without the necessity to check whether in fact an absolute minimum in free energy has been achieved within the mineral subspace included in the simulation.

D.7.3.2.2 Pitzer Activity Coefficient Algorithm. For implementation of the Pitzer model for use in the DOE Science and Technology Modeling program, the GMIN activity coefficient algorithm was adapted for use with the stoichiometric chemical reaction formulation common to reactive transport models. The GMIN code is based on minimization of the Gibbs free energy, which, although mathematically equivalent to the stoichiometric reaction approach for equilibrium systems, involves a different set of numerical algorithms for obtaining the equilibrium state of the system. The need for an stoichiometric-based approach in reactive transport models is dictated by the necessity to describe systems in partial equilibrium. In these systems, kinetically controlled mineral reactions and slowly evolving redox reactions, for example, can control the state of the system. Such reactions are especially important for describing the interaction between the Hanford sediments and the tank fluid.

The Pitzer activity coefficient algorithm is based on a virial expansion (Pitzer 1973, 1991), which reduces to the Debye-Hückel formulation at low ionic strength. The virial expansion involves a sum over all possible binary and ternary short-range interaction terms. The expansion coefficients must be determined through extensive experimental work over a range of pressure and temperature conditions. It is generally not possible to extrapolate results beyond the region used for fitting the data. The Pitzer activity coefficients account for electrostatic interaction and ion hydration effects in addition to formation of complexes and ion pairing. In this sense the Pitzer approach differs conceptually from the Debye-Hückel formulation in which only electrostatic and hydration effects are included. In the Debye-Hückel formulation, complexing and ion pairing must be explicitly taken into account. When using a Debye-Hückel activity coefficient algorithm in speciation calculations any of the relevant chemical species that are found in a thermodynamic database are generally employed. Often many of these species are unimportant, but some are essential. The Pitzer model, in contrast, uses a restricted set of aqueous species compared to the Debye-Hückel model. To determine which additional species are necessary to include in any particular chemical system, the user must refer to the original data on which the expansion coefficients in the Pitzer model are based. Otherwise double counting the effect of species interactions on the activity correction could result. For example, the species $\text{NaCl}_{(\text{aq})}$ is not considered a valid species in the Pitzer model at moderate temperatures, but is usually included in a Debye-Hückel model—although at low temperatures it probably has little effect within the range of validity of the Debye-Hückel algorithm. On the other hand, strong complexes such as $\text{NaNO}_{3(\text{aq})}$ and $\text{NaNO}_{2(\text{aq})}$ are required in both models for an accurate representation of the fluid composition. In addition, species which undergo protonation and deprotonation, such as $\text{H}^+ \text{-OH}^- \text{-H}_2\text{O}$, $\text{CO}_{2(\text{aq})} \text{-CO}_3^{2-} \text{-HCO}_3^-$, $\text{Al}^{3+} \text{-Al(OH)}_4^-$, $\text{Fe}^{3+} \text{-Fe(OH)}_4^-$, and $\text{SiO}_{2(\text{aq})} \text{-H}_3\text{SiO}_4 \text{-H}_2\text{SiO}_4^{2-}$ generally must be explicitly taken into account. Because the activity coefficient in the Pitzer formulation accounts for aqueous complexing and ion pairing, the greater these effects the smaller the activity coefficient, thereby reducing the activity of the free ion or neutral species.

An immediate consequence of the difference between the Pitzer and Debye-Hückel approaches for incorporating speciation, is the effect this has on computation of mineral solubility and retardation, two important chemical processes for reducing the migration of contaminants. In the Debye-Hückel approach it is necessary to explicitly include those complexes that have a significant contribution to the total aqueous concentration of the species in question to properly account for solubility and retardation. In the Pitzer model, **this** is handled somewhat differently depending on whether aqueous complexes are explicitly included in the model or whether their presence is adsorbed into activity coefficients. If complexes are not explicitly included, the reduction in retardation of a particular species is taken into account by a reduction in the activity coefficient of that species. Both models, of course, must give the same results within a common range of validity.

To obtain a sense of the accuracy with which the Pitzer activity coefficient formulation can represent mineral solubility at high ionic strength, comparison is given with experimentally measured data for the solubility of $\text{NaNO}_{3(\text{s})}$, an important component of tank waste. Using the FLOTTRAN code with the GMIN database for Pitzer activity coefficient corrections the results presented in Table D.7.3.1 are obtained. Also listed in the table is the solubility predicted using the Debye-Hückel activity coefficient algorithm. As can be seen from the table, the fit with the Pitzer model is quite good for temperatures above 25 °C. By contrast, the Debye-Hückel model

significantly over predicts the solubility at high temperatures and under predicts it at low temperatures. The GMIN database is calibrated for temperatures at 25 °C and above for this system, which explains the spurious increase in solubility at 20 °C obtained from the Pitzer model. GMIN, in fact, failed to converge for temperatures below approximately 18°C, which illustrates the danger in going outside the range of calibration of the Pitzer expansion coefficients.

Table D.7.3.1. Comparison of the Solubility of NaNO₃ as Computed Using FLOTTRAN with Pitzer and Debye-Hückel Activity Coefficient Corrections, with Experimental Data Taken From Kirk-Othmer Encyclopedia of Chemical Technology Published by Wiley Interscience.

T[°C]	Total Na [Molal]		Experiment [Molal]
	Pitzer	Debye-Hückel	
-17.5			7.4
0.		5.142	8.62
20.	13.919		
25.	10.773	8.838	
40.	12.158	12.806	12.39
80.	17.401	30.298	17.42
100.	21.213	34.126	-
120.	24.486	32.432	24.80

D.7.3.3 Results

In this section reaction path calculations are presented for the equilibrium state of the tank waste inventory using FLOTTRAN combined with the Pitzer algorithm. In what follows, compositions of three tanks in the SX tank farm are evaluated. These are tanks SX-108, SX-109 and SX-I 15. Not all species possible are considered, but only a selected set which constitutes the dominant species in the tank waste and several minor species for which there exists temperature-dependent thermodynamic data. These species are: Al, Fe, Ca, Ni, K, Na, NO₃, NO₂, Cl, CO₂, S, Cr, and Si. Those species not included in the present analysis are: F, Mn, P, Pb, Pu, Se, Sr, Tc, U, Zr, and organic species. However, incorporation of these species should not affect the major solution properties because of their low concentrations.

D.7.3.3.1 Initial Tank Waste Inventory. Initial conditions for the reaction path simulations were determined from the initial total tank waste inventories, including contributions from both liquid and solid phases. The tank inventory at the time of a leak can only be estimated since there are no direct measurements available. The pH of the liquid portion of the tank waste composition is not known, and because of errors involved in the estimation procedure, the waste composition may not be charge balanced. For these reasons it is necessary to make some additional assumptions to determine the initial pH and to obtain an initially balanced solution.

Jones et al. (2000) arbitrarily set the initial OH⁻ concentration to 0.1 mol/L and balanced the solution charge on Na⁺. An alternative approach to that of Jones et al. (2000) is to use the Na⁺ inventory estimated from the HDW model and determine pH by charge balancing on OH⁻. This approach has the advantage that it involves only one adjustable parameter (namely the concentration of OH⁻), whereas the approach used by Jones et al. (2000) involves two parameters (concentrations of OH⁻ and Na⁺). There seems to be no justifiable reason why the HDW calculated Na⁺ concentration should not be used if all the other species concentrations are. This latter approach is followed in this report with the exception of tank SX-108. For this tank it was necessary to use a higher weight percent H₂O than derived from the HDW model by Jones et al. (2000) in order to obtain convergence. The starting solution compositions for tanks SX-108, SX-109, and SX-115 for the reaction path calculations are listed in Table D.7.3.2.

Table D.7.3.2. Initial Tank Waste Inventory for Total Liquid and Solid Contributions Used as Starting Solution in Reaction Path Calculations.

Tank	sx-108	sx-109	sx-115
Temperature [C]	100	100	75
H ₂ O [wt%]	30*(27.11)	31.39	75.07
Species	Total Concentration[mol/L]		
H ₂ O	35.09 ^(a)	29.15	44.09
Al(OH) ₄ ⁻	3.361	2.56	0.8258
Fe(OH) ₄ ⁻	0.0072	0.0056	0.0021 1
Ca ⁺⁺	0.0325	0.0252	0.00950
Ni ⁺⁺	0.00649	0.00504	0.00173
K ⁺	0.0739	0.05763	0.01105
Na ⁺	19.6	15.19	3.593
OH ⁻	5.2502#	3.9645#	0.6172#
NO ₃ ⁻	5.46	4.485	1.197
NO ₂ ⁻	4.42	3.225	0.784
Cl ⁻	0.34	0.2651	0.05071
HCO ₃ ⁻	0.0325	0.0252	0.00955
SO ₄ ⁻⁻	0.0277	0.06775	0.0192
CrO ₄ ⁻⁻	0.4128	0.321 1	0.05088
SiO ₂ (aq)	0.0933	0.06561	0.01279
Cs+&	6.51 ^e -5	4.38e-5	8.35e-6

(a) Assumed value—value in parentheses is reported by Jones et al. (2000). #-Value determined by charge balance. &-Value corresponds to radioisotope Cs¹³⁷.

Note: Values are Taken From Jones et al. (2000), Tables 1a and 1b, Derived from the HDW Model with the Exception of OH that is Determined by Charge Balance. For Tank SX-108 Assumed Weight Fraction for H₂O is Used. Moles of Water are Determined from the Reported H₂O Weight Fraction for Tanks SX-109 and SX-115.

D.7.3.3.2 Equilibrium Tank Supernatant Compositions. To determine the equilibrium configuration for the starting tank inventories listed in Table D.7.3.2, the three tank fluids are reacted with minerals and a limited number of aqueous reactions. Diaspore was taken as a candidate mineral for the stable equilibrium assemblage in the high temperature tank fluid in place of gibbsite, which is often found in low temperature weathering environments. Boehmite was not considered, which is found as a metastable phase in natural systems.

To facilitate convergence, dominant species in solution are chosen as primary species. Thus in place of H^+ , Al^{3+} , Fe^{3+} , HCO_3^- , and $\text{SiO}_{2(\text{aq})}$, the species K^+ , $\text{Al}(\text{OH})_4^-$, $\text{Fe}(\text{OH})_4^-$, CO_3^{2-} , and $\text{H}_2\text{SiO}_4^{2-}$ are chosen as primary species. Mass action equations and kinetic reaction rates are then expressed in terms of these species along with the remaining primary species that are chosen as the free ionic species. Secondary species included in the model calculations are: H^+ , HCO_3^- , $\text{CO}_{2(\text{aq})}$, $\text{CaCO}_{3(\text{aq})}$, Al^{3+} , $\text{NaNO}_{3(\text{aq})}$, $\text{NaNO}_{2(\text{aq})}$, $\text{SiO}_{2(\text{aq})}$, H_3SiO_4^- , HSO_4^- , Fe^{3+} , $\text{O}_{2(\text{aq})}$, and $\text{NH}_{3(\text{aq})}$. The effects of any other ion pairs and complexes must be accounted for by the Pitzer virial expansion coefficients and are incorporated into activity coefficient corrections.

Reaction path results for the equilibrated aqueous solution with starting initial total concentrations given in Table D.7.2.2 using the Pitzer activity coefficient algorithm are presented in Tables D.7.3.3, D.7.3.4, and D.7.3.5 for tanks SX-108, SX-109, and SX-115, respectively. These results should be considered as preliminary. As refinements in thermodynamic data and data for the Pitzer virial expansion become available, including incorporation of properties for additional species, these results can be expected to change in detail, although the gross properties of the supernate composition should be approximately the same. For some species, notably cesium, chromium, and nickel, new data could significantly alter the results presented here.

The tank solution compositions are characterized by the dominant species NaOH - NaNO_3 - NaNO_2 - $\text{Al}(\text{OH})_3$. Tank SX-108 has the most concentrated aqueous solution of the three tanks considered. The aqueous solution is close to saturation with respect to solids NaNO_3 and NaNO_2 , although these solids did not actually precipitate out in the equilibrium state. Tank SX-109 is also close to saturation with respect to these solids, but with a saturation index an order of magnitude less compared to tank SX-108. Ionic strengths ranged from 18 mol/kg- H_2O for tank SX-108, 17 mol/kg- H_2O for tank SX-109, and to 3.54 mol/kg- H_2O for tank SX-115. Computed solution densities ranged from 2.1 g/cm³ for tank SX-108, 1.65 g/cm³ for tank SX-109, and to 1.13 g/cm³ for tank SX-115. The concentration of Na^+ is higher for tanks SX-108 and SX-109 than the value given in Table D.7.3.1 for the solubility of NaNO_3 , but it should be kept in mind that the solubility is based on equal total concentrations of Na^+ and NO_3^- , which does not apply to the tank inventory. The equilibrium solution compositions were all mildly reducing ($E_h = -0.05$ to -0.227 V) determined by the redox couple NO_3^- and NO_2^- . The pH ranged from approximately 14.11 for tank SX-108, 14.04 for tank SX-109, and to 12.8 for tank SX-115.

**Table D.7.3.3. Final Equilibrium State for Tank SX-108
with Pitzer Activity Corrections. (4 Sheets)**

Temperature [C] = 1.0000E+02

H2O mole fraction = 5.39903-01, weight fraction = 3.04163-01

activity of water = 3.4719E-01

osmotic coefficient = 1.2414E+00

ionic strength = 1.8021E+01

solution density = 2.0924 [g/cm³]

pH = 14.110 pe = -2.941 Eh = -2.17733-01 [V]

primary species	molarity	tot [mol/L]	molality	tot [mol/kg]	act. coef.
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Al (OH)4-	3.2692E+00	3.2692E+00	5.1369E+00	5.1369E+00	1.17223-01
Fe (OH)4-	1.3991E-08	1.3991E-08	2.1985E-08	2.1985E-08	1.70463-01
Ca++	6.3214E-06	6.3223E-06	9.9328E-06	9.93423-06	5.7686E-05
Ni++	1.6286E-15	1.6286E-15	2.5590E-15	2.5590E-15	3.13633-04
K+	7.39003-02	7.3900E-02	1.1612E-01	1.1612E-01	1.5791E+00
Na+	1.0922E+01	1.9508E+01	1.7162E+01	3.0653E+01	1.1312E+00
OH-	5.1469E+00	5.1469E+00	8.0873E+00	8.0873E+00	3.0454E+00
NO3-	2.19423-01	5.4600E+00	3.4478E-01	8.5794E+00	7.1761E+00
NO2-	1.0743E+00	4.4200E+00	1.6881E+00	6.9452E+00	3.5848E+00
Cl-	3.40003-01	3.4000E-01	5.3425E-01	5.34253-01	3.4661E-01
CO3--	3.25003-02	3.2500E-02	5.1068E-02	5.1068E-02	3.5812E-03
SO4--	2.77003-02	2.7700E-02	4.3525E-02	4.35253-02	2.1583E-04
CrO4--	4.12803-01	4.1280E-01	6.48643-01	6.4864E-01	6.3291E-03
H2SiO4--	4.1714E-05	4.3949E-05	6.55463-05	6.90573-05	5.7504E+00

**Table D.7.3.3. Final Equilibrium State for the Tank SX-108
with Pitzer Activity Corrections. (4 Sheets)**

CS+	6.51003-05	6.51003-05	1.02293-04	1.0229E-04	1.4259E+00
H2O	3.5326E+01	3.5326E+01	5.5508E+01	5.5508E+01	1.0000E+00

complex	molarity	molality	act.	coef.	log K
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NaNO3 (aq)	5.2406	8.2346	1.3819		-0.62538
NaNO2 (aq)	3.3457	5.2571	1.0435		-1.3307
H3SiO4 -	2.233663-06	3.509773-06	0.60733		-0.39666
HC03 -	4.541873-08	7.13670E-08	0.24347		-2.1713
siO2(aq)	1.106563-09	1.73875E-09	9.70835E-02		-3.5660
CaCO3 (aq)	9.006683-10	1.41523E-09	1.0000		4.1305
NH3 (aq)	2.080483-14	3.269093-14	1.0000		-13.122
H+	9.81381E-15	1.54206E-14	0.50319		-12.259
HS04-	6.54809E-17	1.02891E-16	0.71615		-9.2546
CO2 (aq)	1.94029E-17	3.04880E-17	31.416		-8.0386
O2(aq)	3.251173-25	5.10860E-25	1.0000		-23.515
Al+++	5.000503-28	7.85734E-28	7.366173-12		-32.451
Fe+++	6.85462E-35	1.077073-34	4.029673-12		-31.370

mineral	volume fraction	concentration	rate [mol/dm^3/s]
		[mol/L]	

Nepheline	4.97243-03	9.1810E-02	0.0000E+00
Portlandite	1.07413-03	3.2494E-02	-3.79693-21
Ni2SiO4	6.1681E-05	1.4476E-03	0.0000E+00
Trevorite	1.8055E-03	3.61113-03	0.0000E+00

**Table D.7.3.3. Final Equilibrium State for Tank SX-108
with Pitzer Activity Corrections. (4 Sheets)**

mineral saturation indices

mineral	SI	log K
<hr/>		
Ni ₂ SiO ₄	0.00000E+00	3.59130E+01
Trevorite	0.00000E+00	3.31103E+01
Nepheline	0.00000E+00	4.21999E+00
Portlandite	0.00000E+00	6.45896E+00
Diaspore	-5.459883-02	1.09772E+00
NaNO ₂ (s)	-7.06677E-02	-2.14063E+00
NaNO ₃ (s)	-8.085703-02	-1.76237E+00
Ni (OH) 2	-3.10092E-01	1.50025E+01
Boehmite	-3.494593-01	8.02859E-01
Halite	-1.01748E+00	-1.57316E+00
Gibbsite	-1.28256E+00	3.291933-01
Thenardite	-1.73667E+00	7.14285E-01
Goethite	-2.33614E+00	7.02211E+00
Calcite	-3.66061E+00	9.31908E+00
Dawsonite	-5.01541E+00	4.37532E-01
Analcime	-5.57853E+00	5.63528E+00
Jadeite	-5.91453E+00	4.51211E+00
Quartz	-6.69584E+00	-4.89194E-01
SiO ₂ (am)	-7.58976E+00	-1.38311E+00
Gypsum	-1.02746E+01	4.91328E+00
Muscovite	-1.06158E+01	1.03469E+01
K-Feldspar	-1.09181E+01	7.73998E+00

**Table D.7.3.3. Final Equilibrium State for Tank SX-108
with Pitzer Activity Corrections. (4 Sheets)**

Paragonite	-1.14430E+01	7.49495E+00	
Kaolinite	-1.46121E+01	5.652753- 01	
gas	log partial pressure	pressure [bars]	log K

co2(g)	-13.05	8.9319E- 14	-6.0689
o2(g)	-21.19	6.52343- 22	-20.409

**Table D.7.3.4. Final Equilibrium State for Tank SX-109
with Pitzer Activity Corrections. (4 Sheets)**

Temperature [C] = 1.0000E+02
H2O mole fraction = 5.57963-01, weight fraction = 3.2228E-01
activity of water = 3.6293E-01
osmotic coefficient = 1.2793E+00
ionic strength = 1.6988E+01
solution density = 1.6504 [g/cm³]
pH = 14.039 pe = -2.834 Eh = -2.09803-01 [V]

primary species	molarity	tot [mol/L]	molality	tot [mol/kg]	act. coef.
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Al (OH) 4-	2.2929E+00	2.2929E+00	4.3109E+00	4.3109E+00	1.4705E-01
Fe (OH) 4-	9.6650E-09	9.6650E-09	1.8171E-08	1.8171E-08	1.9796E-01
Ca++	4.72653-06	4.7275E-06	8.8864E-06	8.8883E-06	8.1746E-05
Ni++	1.2567E-15	1.2567E-15	2.3628E-15	2.3628E-15	4.4024E-04
K+	5.7630E-02	5.7630E-02	1.08353-01	1.08353-01	1.5185E+00
Na+	8.5636E+00	1.5126E+01	1.6101E+01	2.8438E+01	1.1969E+00
OH-	4.0870E+00	4.0870E+00	7.6842E+00	7.6842E+00	2.8466E+00
NO3-	2.3753E-01	4.4850E+00	4.4659E-01	8.4324E+00	5.3257E+00
NO2-	9.10473-01	3.2250E+00	1.7118E+00	6.0634E+00	2.8753E+00
Cl-	2.65103-01	2.6510E-01	4.9842E-01	4.9842E-01	3.82013-01
CO3--	2.52003-02	2.5200E-02	4.7379E-02	4.73793-02	4.1075E-03
SO4--	6.77503-02	6.7750E-02	1.2738E-01	1.2738E-01	3.42023-04
CrO4--	3.2110E-01	3.2110E-01	6.0371E-01	6.0371E-01	6.70603-03
H2SiO4--	4.4788E-05	4.6654E-05	8.4207E-05	8.7715E-05	3.6916E+00

**Table D.7.3.4. Final Equilibrium State for Tank SX-109
with Pitzer Activity Corrections. (4 Sheets)**

Cs+	4.3770E-05	4.3770E-05	8.2293E-05	8.2293E-05	1.3447E+00
H2O	2.9524E+01	2.9524E+01	5.5508E+01	5.5508E+01	1.0000E+00

complex	molarity	molality	act.	coef.	log K
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NaNO3 (aq)	4.2475	7.9858	1.3598		-0.62538
NaNO2 (aq)	2.3145	4.3516	1.0178		-1.3307
H3SiO4 -	1.86508E-06	3.506593E-06	0.59009		-0.39666
HC03-	4.65612E-08	8.75413E-08	0.24861		-2.1713
CaCO3 (aq)	1.015513E-09	1.909303E-09	1.0000		4.1305
SiO2(aq)	7.955263E-10	1.49569E-09	0.11801		-3.5660
NH3(aq)	1.05388E-14	1.98144E-14	1.0000		-13.122
H+	9.21028E-15	1.731663E-14	0.52741		-12.259
HS04-	3.109763E-16	5.84677E-16	0.68791		-9.2546
CO2(aq)	2.78316E-17	5.232713E-17	25.814		-8.0386
O2(aq)	3.795653E-25	7.136323E-25	1.0000		-23.515
Al+++	3.16433E-28	5.94937E-28	1.64618E-11		-32.451
Fe+++	4.76373E-35	8.95645E-35	7.47622E-12		-31.370

mineral	volume fraction	concentration rate [mol/dm ³ /s]
		[mol/L]

Diaspore	3.59923E-03	2.02663E-01 0.0000E+00
Nepheline	3.4907E-03	6.4452E-02 3.79693E-21
Portlandite	8.3286E-04	2.5195E-02 0.0000E+00
Ni2SiO4	4.7563E-05	1.1162E-03 0.0000E+00
Trevorite	1.4028E-03	2.8055E-03 6.07503E-24

**Table D.7.3.4. Final Equilibrium State for Tank SX-109
with Pitzer Activity Corrections. (4 Sheets)**

mineral saturation indices		
mineral	SI	log K
Ni ₂ SiO ₄	0.00000E+00	3.59130E+01
Trevorite	0.00000E+00	3.31103E+01
Diaspore	0.00000E+00	1.09772E+00
Nepheline	0.00000E+00	4.21999E+00
Portlandite	0.00000E+00	6.45896E+00
NaNO ₃ (s)	-1.01184E-01	-1.76237E+00
NaNO ₂ (s)	-1.63581E-01	-2.14063E+00
Boehmite	-2.94860E-01	8.028593-01
Ni(OH) ₂	-3.00520E-01	1.50025E+01
Halite	-1.00858E+00	-1.57316E+00
Thenardite	-1.07676E+00	7.14285E-01
Gibbsite	-1.20871E+00	3.291933-01
Goethite	-2.32167E+00	7.02211E+00
Calcite	-3.53056E+00	9.31908E+00
Analcime	-5.53836E+00	5.63528E+00
Quartz	-6.67647E+00	-4.89194E-01
SiO ₂ (am)	-7.57039E+00	-1.38311E+00
Gypsum	-9.46674E+00	4.91328E+00
Muscovite	-1.05118E+01	1.03469E+01
K-Feldspar	-1.09232E+01	7.73998E+00
Kaolinite	-1.44449E+01	5.652753-01

**Table D.7.3.4. Final Equilibrium State for Tank SX-109
with Pitzer Activity Corrections. (4 Sheets)**

gas	log partial pressure	pressure [bars]	log K

c02(g)	-12.90	1.25963-13	-6.0689
O2(g)	-21.04	9.1127E-22	-20.409

**Table D.7.3.5. Final Equilibrium State for Tank SX-115
with Pitzer Activity Corrections. (4 Sheets)**

Temperature [C]	= 7.5000E+01				
H2O mole fraction	= 8.8313E-01, weight fraction = 7.9297E-01				
activity of water	= 8.6911E-01				
osmotic coefficient	= 1.0601E+00				
ionic strength	= 3.5377E+00				
solution density	= 1.1326 [g/cm^3]				
pH = 12.836	pe = -0.6980	Eh = -4.8214E-02 [V]			
.....					
primary species	molarity	tot [mol/L]	molality	tot [mol/kg]	act. coef.

Al (OH) 4-	8.00323-02	8.00323-02	8.91143-02	8.9114E-02	5.70083-01
Fe (OH) 4-	7.5584E-09	7.5584E-09	8.4160E-09	8.4160E-09	5.1622E-01
Ca++	5.1707E-05	5.3061E-05	5.7574E-05	5.9081E-05	1.05523-02
Ni++	1.3837E-15	1.3837E-15	1.5407E-15	1.54073-15	2.3441E-02
K+	1.10513-02	1.1051E-02	1.23053-02	1.23053-02	4.8143E-01
Na+	3.0741E+00	3.5930E+00	3.4229E+00	4.0007E+00	7.3812E-01
OH-	1.3084E+00	1.3082E+00	1.4569E+00	1.4566E+00	8.04223-01
NO3-	7.50523-01	1.1970E+00	8.3568E-01	1.3328E+00	7.6596E-01
NO2-	7.11493-01	7.84003-01	7.9222E-01	8.7296E-01	6.0563E-01
Cl-	5.07103-02	5.07103-02	5.6464E-02	5.64643-02	5.9338E-01
CO3--	9.5493E-03	9.5521E-03	1.06333-02	1.06363-02	3.2931E-02
SO4--	1.92003-02	1.92003-02	2.13793-02	2.13793-02	1.94093-02
CrO4--	5.08803-02	5.08803-02	5.6653E-02	5.66533-02	2.47213-02
H2SiO4--	1.22923-02	1.2498E-02	1.36863-02	1.3916E-02	4.03743-02

**Table D.7.3.5. Final Equilibrium State for Tank SX-115
with Pitzer Activity Corrections. (4 Sheets)**

CS+	8.3450E-06	8.3450E-06	9.2920E-06	9.2920E-06	4.53523-01
H2O	4.9852E+01	4.9852E+01	5.5508E+01	5.5509E+01	1.0000E+00
complex	molarity	molality	act.	coef.	log K

NaNO3 (aq)	0.44648	0.49714	1.0600	-0.48697	
NaNO2 (aq)	7.25094E-02	8.07371E-02	0.92268	-1.2114	
H3SiO4 -	2.06453E-04	2.29880E-04	0.46978	-0.57927	
HCO3-	1.43903E-06	1.60232E-06	0.39961	-2.6081	
CaCO3 (aq)	1.35393E-06	1.50756E-06	1.0000	3.8505	
SiO2 (aq)	5.28990E-08	5.89015E-08	0.72473	-3.9745	
H+	2.66693E-13	2.96955E-13	0.49070	-12.707	
CO2 (aq)	9.57401E-14	1.06604E-13	1.9926	-9.0185	
HSO4-	4.43485E-14	4.93808E-14	0.54604	-10.057	
NH3 (aq)	2.35176E-15	2.61861E-15	1.0000	-13.697	
O2 (aq)	4.60580E-26	5.12843E-26	1.0000	-25.540	
Al+++	1.87913E-29	2.09236E-29	4.48986E-06	-32.458	
Fe+++	3.36743E-35	3.74953E-35	4.06825E-07	-32.179	
mineral	volume fraction	concentration rate [mol/dm^3/s]			
		[mol/L]			

Diaspore	1.3246E-02	7.4581E-01	0.0000E+00		
Portlandite	3.1241E-04	9.4510E-03	0.0000E+00		
Ni2SiO4	1.4404E-05	3.3805E-04	0.0000E+00		
Trevorite	5.2795E-04	1.0559E-03	0.0000E+00		

**Table D.7.3.5. Final Equilibrium State for Tank SX-115
with Pitzer Activity Corrections. (4 Sheets)**

mineral saturation indices

mineral	SI	log K

Ni ₂ SiO ₄	0.00000E+00	3.58827E+01
Trevorite	0.00000E+00	3.29227E+01
Diaspore	0.00000E+00	1.30199E+00
Portlandite	0.00000E+00	6.07884E+00
Nepheline	-3.592453-02	4.12903E+00
Boehmite	-3.27748E-01	9.74242E-01
Calcite	-6.884103-01	8.98377E+00
Gibbsite	-8.03015E-01	5.599033-01
Ni(OH) ₂	-1.29819E+00	1.50065E+01
NaNO ₃ (s)	-1.37923E+00	-1.58799E+00
Goethite	-1.41880E+00	6.95113E+00
NaNO ₂ (s)	-1.95153E+00	-2.03510E+00
Thenardite	-2.04069E+00	5.362893-01
Analcime	-2.17217E+00	5.55394E+00
Halite	-2.67820E+00	-1.60582E+00
Quartz	-4.06685E+00	-6.716463-01
Gypsum	-5.00658E+00	4.71372E+00
SiO ₂ (am)	-5.06146E+00	-1.66625E+00
Muscovite	-5.43289E+00	1.07564E+01
K-Feldspar	-5.85629E+00	7.72899E+00
Kaolinite	-8.79011E+00	6.65214E-01
gas	log partial pressure	pressure [bars] log K

**Table D.7.3.5. Final Equilibrium State for Tank SX-115
with Pitzer Activity Corrections. (4 Sheets)**

CO ₂ (g)	-10.80	1.58143-11	-7.1467
O ₂ (g)	-22.20	6.3531E-23	-22.447

There are two general observations that can be made regarding the derived supernate compositions. First, molality (mol/kg H₂O) and molarity (mol/L) differ significantly from each other for the high ionic strength fluids because of the reduced amount of H₂O present. Second, species activity may be very different from concentration (molality), in some cases by many orders of magnitude for higher valent species. For example the calculated activity coefficients for tank SX-108 for Ca²⁺ and SO₄²⁻ are 5.7686e-5 and 2.1583e-4, respectively, which could indicate the presence of significant ion pairing not explicitly incorporated in the Pitzer formulation. It is interesting to note that the cesium activity coefficient increases with increasing ionic strength, as can be seen by comparing the results for the different *tank* compositions. If ion pairing with cesium was important, it is expected that the cesium activity coefficient would decrease rather than increase.

Nepheline (NaAlSi₃O₈) formed in tanks SX-108 and SX-109, and was close to saturation in tank SX-115 but did not precipitate. The mineral diasporite is slightly undersaturated in tank SX-108, but saturated in tanks SX-109 and SX-115. This is presumably because somewhat more nepheline precipitated in tank SX-108 thereby reducing the concentration of aluminum. However, it is also possible that if the HDW calculated weight percent of H₂O could have been used, diasporite would also have been saturated in tank SX-108. Portlandite [Ca(OH)₂], and nickel bearing minerals Ni₂SiO₄, and trevorite (NiFe₂O₄) precipitated in all three tanks. Other aluminosilicate minerals are undersaturated as a result of the high pH and low silica concentration as demonstrated by the saturation indices presented in the tables, in spite of rather high aluminum concentrations remaining in solution. It is interesting to note that solids NaNO_{3(s)} and NaNO_{2(s)} are approximately saturated in the predicted tanks SX-108 and SX-109 liquid phases, and undersaturated in the tank SX-115 liquid.

The calculations predict that Ni²⁺ completely precipitates from solution in the form of Ni₂SiO₄ and trevorite (although the mineral Ni₂SiO₄ would not be expected to form at these low temperatures). However, this could be an artifact of the lack of nickel complexes, such as NiOH⁺, which were not included in the calculation because of unavailability of thermodynamic data at elevated temperatures. Chromium remains in solution at its initial value. No solid phases could be found which precipitated out chromium and thermodynamic data for speciation of chromium in different redox states was also not available at elevated temperatures.

The sensitivity of the pH of the final equilibrium state on the initial pH is illustrated in Table D.7.3.6 for tank SX-115. As can be seen from the table, for low initial pH the final pH is roughly the same, controlled primarily by mineral reactions and is insensitive to the initial pH used in the reaction path calculation. The sodium concentration is determined by charge balance, and so must increase as the O K concentration increases. This is an important result because it indicates that the final equilibrium state is largely controlled by reaction with solids. It would thus appear to be important to determine the solid composition of the tank waste in order to provide a better estimate of the composition of the liquid phase.

Table D.7.3.6. Sensitivity of Final pH, Eh, and Ionic Strength on the Initial OH⁻ Concentration for Tank SX-115.

Initial OH ⁻ [mol/L]	Initial pH	Final pH	Total Na ⁺ [mol/L]	Eh [V]	Ionic Strength [mol/kg H ₂ O]
5.0	13.347	13.381	8.0108	-0.887	5.1449
1.0	12.720	12.943	4.0106	-0.559	3.7552
0.6172	12.494	12.836	3.5930	-0.482	3.5377
0.1	11.739	12.660	3.1087	-0.356	3.2526
0.001	9.7429	12.605	2.9956	-0.316	3.1783
0.00001	7.7441	12.595	2.9768	-0.309	3.1663

The Debye-Hückel activity correction model gave qualitatively similar results as the Pitzer model for the tank **SX-115** composition. The predicted equilibrium pH was approximately the same, and with the exception of calcite that formed in the Debye-Hückel model, the same stable mineral assemblage formed. However, the fluid composition **was** quantitatively different and the amounts of minerals that precipitated was also different between the two activity coefficient models.

Temperature was found to be an important factor in determining the liquid equilibrium concentration. Attempting to perform reaction path calculations at **25 °C** led to unrealistically high pH values on the order of 15 or greater.

D.7.3.3.3 Comparison with Jones et al. (2000). Jones et al. (2000) used the computer code ESP, from OLI Systems, to calculate tank supernate compositions. The ESP code is proprietary software, which makes it difficult to obtain a deeper understanding of the algorithms and origin of databases used by the code and to more fully understand its computed results. Felmy (2000) noted certain problems with the ESP database in comparison with the code GMIN when analyzing several different waste forms. In addition to differences in thermodynamic data, there are undoubtedly also differences in the activity coefficient algorithms used by the two codes that could lead to different supernate compositions.

Although the same tank waste inventories are used in this study as in Jones et al. (2000), because of the different approaches used for determining charge balance and the concentration of OH⁻, the compositions presented in this study are more concentrated than the results presented by Jones et al. (2000). It should also be noted that there appears to be a discrepancy in overall mass balance in the results presented by Jones et al. (2000), although it is not clear if this was caused by an incorrect labeling of the concentration units as molarity rather than molality.

Calculations were also carried out with FLOTTRAN using the prescription for charge balance and OH⁻ concentration suggested by Jones et al. (2000). There were several differences in the results presented by Jones et al. (2000) using the ESP code. Thenardite (Na₂SO₄), goethite (FeOOH), and calcite (CaCO₃) were predicted by Jones et al. (2000) to form, but remained undersaturated in the FLOTTRAN simulations. In place of Ni(OH)₂, FLOTTRAN predicted a nickel silicate

(Ni_2SiO_4) and trevorite to form, although as noted above Ni_2SiO_4 is only expected to form at higher temperatures.

D.7.3.3.4 Important Uncertainties. Because of the large uncertainties involved, both in the reaction path calculation itself resulting from uncertainty in thermodynamic data and activity corrections, and in the HDW derived initial tank waste inventory, these calculations can only be viewed at best as rough estimates of the composition of the leaking tank fluid. Limitations exist on the availability of thermodynamic data for minerals and aqueous species, and activity coefficient correlation data for use in the Pitzer model over the range of temperatures needed. In addition, uncertainties arise from the possibility of nucleation kinetics inhibiting mineral reactions even if thermodynamically feasible (such as formation of Ni_2SiO_4 noted above). In this regard, knowledge of the actual minerals that have formed in the tanks would be useful in validating the model predictions. It is emphasized that the final equilibrium state is independent of the kinetic rates used in the real-time reaction path calculations presented here, and therefore these values play no role in the uncertainty of the simulations.

Perhaps the greatest uncertainty in these calculations is the estimate of the initial tank waste inventory. Agnew and Corbin (1998, Table 4), for example, derived waste inventories for several tanks including tank SX-108. The inventory they estimated for tank SX-108 resulted in a significantly lower Na^+ concentration compared to that calculated by Jones et al. (2000), which resulted in a slightly acidic starting pH. The final pH, however, was still above 12 as a result of mineral precipitation reactions. Apparently, Agnew and Corbin (1998) derived their results by averaging predicted inventories from a number of tanks over some period in time (Tom Jones, private communication), whereas Jones et al. (2000) attempted to obtain each specific tank inventory at the most probable time the tank leaked. Much work still remains to be done to resolve discrepancies between different authors and to obtain representative tank supernate compositions that can be used for modeling migration of radionuclides in the vadose zone.

It will be difficult to observe fluids in the vadose zone with compositions directly comparable to the tank fluids because of various physical and chemical effects that could either dilute or concentrate them. Mixing with ambient pore water and infiltrating surface water will result in dilution. Changes in chemical composition can also be expected as a result of interaction of the leaked tank fluid with sediment minerals. Concentration could occur due to evaporative effects caused by the heat released from the high temperature tanks such as tanks SX-108 and SX-109.

Finally, in order to integrate the tank supernate compositions derived here with reactive transport simulations, it is also necessary to provide an equation of state for the fluid density and constitute relation for viscosity as functions of temperature, pressure and composition. There exist equations of state for simplified systems involving NaCl and NaNO_3 , but not for the multicomponent fluids of enormous complexity, which have leaked from some of the Hanford storage tanks.

D.7.3.4 Conclusions and Implications

The calculations for the supernate tank fluid presented in this contribution suggest that extremely high ionic strength fluids have leaked from several of the tanks in the SX tank farm. The high sodium concentration associated with these fluids could help explain the advanced migration of

cesium that has been observed in the vadose zone beneath tank SX-108. Further work and field investigations are required to understand the effect these fluids have had on alteration of the Hanford sediments and their effect on retardation of radionuclides in the vadose zone.

D.7.3.5 References

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D.7.4 EVALUATION OF THE FIELD EXCHANGE CAPACITY OF HANFORD SEDIMENTS WITH IMPLICATIONS FOR ^{137}Cs MIGRATION

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D.7.4.1 Introduction

While the ion exchange parameters extracted from the batch experiments of Zachara et al. (2001) (Section D.3.1) and the column experiments of Carroll et al. (2001) (Section D.3.3) provide an excellent basis for modeling cesium reactive transport under experimental conditions, it remains to be demonstrated that the same ion exchange model is capable of describing cesium transport in the field. The eventual goal of the modeling of the field transport of cesium is twofold. First, to understand the processes taking place at tanks like tank SX-108 where cesium penetration to significant depths is observed, and second, to use this new-found understanding for improved scientifically credible predictions of future behavior. The leak volume and duration at tank SX-108, however, is poorly known, and the interpretation of cesium migration is complicated by the effects of coupled processes like in-tank boiling and subsurface mineral alteration. In contrast, the volume and duration of the tank SX-115 leak is well known. Tank SX-115 was below boiling when the leak occurred in 1965 over a 1-week period and the tank remained below boiling subsequently. A borehole, 299-W23-19, (R. S. Serne, personal communication 2001) was sited within about 2 m of the edge of tank SX-115, close to the location of the largest of three leaks developed below this tank (Raymond and Shdo 1966). Through analysis of water extractable ions, Serne (personal communication 2001) identified a well-defined chromatographic separation of cations in 299-W23-19 borehole that can be attributed to the ion exchange of waste-derived cations. A peak of sodium occurred at shallower depths in the borehole and is clearly separated from calcium and magnesium peaks which occurred at greater depth. Technetium and nitrate, apparently acting as nonreactive tracers, coincided approximately with the calcium and magnesium fronts. Cesium was not detected in the W23-19 borehole, but was encountered in shallow horizontal wells drilled directly below tank SX-115 (Raymond and Shdo 1966).

Although there is little direct interest in sodium, calcium, magnesium, and potassium as contaminants, these cations are very useful in establishing whether the multicomponent ion exchange model developed to describe cesium exchange and transport in the batch and column experiments can be applied to the field. A key question is whether the *effective* exchange capacity of the Hanford sediments is the same as that measured in batch and column experiments, or whether various hydrologic physical processes may have caused a reduction in cesium retardation. By *effective* exchange capacity, we are referring *not* to the CEC determined with conventional analytical methods (e.g., ^{22}Na isotopic dilution), but rather to the effective CEC needed to account for the observed chromatographic separation (if any) of the cations in the field setting. By applying the self-consistent, multicomponent cation exchange model developed for the column experiments (Carroll et al. 2001) to the distribution of the cations sodium,

calcium, potassium, magnesium, and cesium below tank SX-115, we can make a direct comparison of the laboratory and field effective exchange capacities.

D.7.4.2 Determination of Ion Exchange Parameters

Ion exchange parameters were determined by fitting CECs and ion selectivity coefficients to both the batch experimental data of Zachara et al. (2001) (Section D.3.1) and to the column data of Carroll et al. (2001) (Section D.3.3). The fitting procedure used a strong weighting of the column experiments so as to favor these results where the batch and column results were in conflict (see discussion in Carroll et al. 2001). The fitting was carried out with the general optimization code PEST used in conjunction with speciation calculations carried out by CRUNCH. In this way, the resulting parameter set is fully compatible with the reactive transport simulations of cesium migration in both the column experiments and the field which were also carried out with CRUNCH. In contrast to the fit of the data presented by Zachara et al. (2001), the fits presented here include both activity coefficient corrections and aqueous complexation as described further below. Equally important, however, was the inclusion of batch experimental data on the Cs-Na, Cs-Ca, and Cs-K binary systems (Zachara et al. 2001) and a Cs-Na-K column experiment (Carroll et al. 2001) in a single global optimization to arrive at a consistent set of numbers that can be used to describe the multicomponent system.

The selectivity coefficients in Table D.7.4.1 were fit assuming the Gapon activity convention:

where M is the exchanging cation (Na^+ , K^+ , Ca^{2+}), and m is its charge (Appelo and Postma 1996). The exchange reactions can then be used to write a standard mass action equation for binary Cs-M exchange:

$$K_{\text{M/Cs}} = \frac{[\text{M}_{1/m}\text{X}][\text{Cs}^+]}{[\text{CsX}][\text{M}]^{1/m}} \quad (\text{D.7.4.2})$$

In agreement with the conclusions of Zachara et al. (2001), multiple exchange sites were needed to capture the large range in the cesium K_d as a function of cesium concentration. We have fitted cesium exchange with a three-site model because it provides a substantially better fit of the Cs-Ca and, to a lesser extent, the Cs-Na exchange data. The three-site model was used because of the improvement it gave in matching the batch data; however, there is no clear physical evidence for more than two distinct sites actually present in the Hanford sediments.

Table D.7.4.1. Cesium Exchange Selectivity Coefficients, Ion Pair Formation Constants, and CECs Derived From Fits of Batch and Column Experiments, with Weighting of Column Exchange Experiments.

Exchange Reaction	Fitted Parameters Log K
$\text{NaX1} + \text{Cs}^+ = \text{Na}^+ + \text{CsX1}$	6.85
$\text{NaX2} + \text{Cs}^+ = \text{Na}^+ + \text{CsX2}$	3.00
$\text{NaX3} + \text{Cs}^+ = \text{Na}^+ + \text{CsX3}$	2.10
$\text{KX1} + \text{Cs}^+ = \text{K}^+ + \text{CsX1}$	4.50
$\text{KX2} + \text{Cs}^+ = \text{K}^+ + \text{CsX2}$	3.77
$\text{KX3} + \text{Cs}^+ = \text{K}^+ + \text{CsX3}$	0.70
$\text{Ca}_{0.5}\text{X1} + \text{Cs}^+ = 0.5\text{Ca}^{2+} + \text{CsX1}$	7.13
$\text{Ca}_{0.5}\text{X2} + \text{Cs}^+ = 0.5\text{Ca}^{2+} + \text{CsX2}$	6.46
$\text{Ca}_{0.5}\text{X3} + \text{Cs}^+ = 0.5\text{Ca}^{2+} + \text{CsX3}$	1.58
Ion Pairs	Effective Log K (fitted)
$\text{NaNO}_3(\text{aq}) \rightarrow \text{Na}^+ + \text{NO}_3^-$	0.26
$\text{CsNO}_3(\text{aq}) \rightarrow \text{Cs}^+ + \text{NO}_3^-$	0.50
Bdot parameter (Cs-X)	-8.90E-02
Exchange Site	CEC ($\mu\text{eq g}^{-1}$)
Site 1	0.037
Site 2	0.14
Site 3	102

We chose to fit the CEC rather than using an independently determined value because there is significant uncertainty in the CEC determined for these Hanford sediments. The highest value for the CEC was determined by cation elution during preliminary washes of the sediment (CEC = 138 $\mu\text{eq/g}$) (Carroll et al. 2001). Lower values of the CEC were determined by ^{22}Na and ^{45}Ca isotopic equilibrium measurements (CEC = 46 $\pm$ 3 $\mu\text{eq/g}$) (Zachara et al. 2001; Carroll et al. 2001). More important than the uncertainty associated with the CEC, however, is the fact that CEC determinations for different cations give different values. For describing multicomponent ion exchange in the field, it is essential to arrive at a single set of CEC(s). Except for the low value of 46 $\mu\text{eq/g}$ (this value results in a poor fit of the experimental data at high cesium concentrations), any of the other CEC values could have been used as a constraint in the fitting procedure. This is because the combined fit of CECs and selectivity coefficients is not unique as shown by the strong inverse correlation between selectivity coefficients for a particular site and the CEC of that site. It is the combination of CECs and selectivity coefficients that control the migration rate of the various cations rather than one parameter or another acting by itself.

The important point, therefore, is to use a *combined* set of CECs and selectivity coefficients that match the results of the batch and column experiments.

We used a standard Debye-Huckel formulation for activity coefficients augmented with fitting parameters for ion pair formation to describe solution activities accurately in the highly concentrated and variable Hanford system. Free cation activities were calculated by adjusting the effective log Ks for the ion pairs $\text{CsNO}_{3(aq)}$, $\text{Ca(NO}_3)_2(aq)$, and $\text{NaNO}_{3(aq)}$ to match free cation activities determined with the Pitzer approach as implemented in the code GMIN (Felmy 1995). In this approach, the effective log Ks for the ion pairs attempt to capture the effect of *both* the specific ion pair log K in the GMIN database (not the same *as* the effective log K proposed here) *and* the parameters describing the cation-anion interaction (the interaction parameters) in the Pitzer formulation. This was carried out in practice by treating the GMIN-calculated ion activities at 0.1, 1, and 5 M NaNO_3 as data which must be honored in the optimization procedure. Using this approach, we were able to simulate quite closely the species activities (not activity coefficients) calculated with the Pitzer approach up to 5 M NaNO_3 . It is unclear, however, whether this approach can be extended significantly beyond 5M NaNO_3 . In terms of ion exchange, however, the most important quantity is the *ratio* of activity corrections (for example, Na^+ to Cs^+) and not the absolute magnitude of the correction.

It was also necessary to include an empirical activity coefficient correction for the various Cs exchange species in order to capture the ionic strength dependence of the exchange. This took the form of a standard "Bdot" correction in the extended Debye-Huckel equation, but *was* applied only to the exchange species activities:

$$\ln \gamma_{\text{Cs-X}} = \text{BI} \quad (\text{D.7.4.3})$$

D.7.4.3 Multiphase Flow, Heat Transport, and Reactive Transport Simulations of the Tank SX-115 Leak

The tank SX-115 leak and subsequent plume migration through the vadose zone was modeled by coupling the reactive transport code CRUNCH to the multiphase flow and heat transport code NUFT (Nitao 1998). CRUNCH reads in a transient flow, liquid saturation, and temperature fields generated by NUFT. The simulation begins in 1959 when tank SX-115 was constructed and ends in the year 1999 when borehole 299-W23-19 was drilled. NUFT was run for 10,000 years prior to the emplacement of the tank using a constant infiltration rate of 100 mm/yr to obtain a steady-state initial flow field and liquid saturation. A three-dimensional grid was considered to be necessary to capture the potential effects of a dipping gravel layer *and* the lack of symmetry with respect to the large leak located on the edge of the tank near borehole 299-W23-19. Nineteen and 17 cells of 2.33-m spacing were used in the X and Y direction respectively, while 34 cells of 2-m spacing were used in the Z (vertical) direction. Tank SX-115 was maintained at a constant temperature of 70 °C throughout the period of the simulation (1959-1999). The data of Raymond and Shdo (1966) indicate that three distinct leaks developed below tank SX-115 (Figure D.7.4.1). Although it is not clear that all three leaks occurred during the same 1-week period in 1965, we have assumed that the largest of the leaks developed on the edge of the tank near well 299-W23-19 (the only one we have modeled) and consisted of 22,800 gallons, which 40% of the total 57,000 gallons lost during this period.

Figure D.7.4.1. Distribution of Contamination Below Tank SX-115 (from Raymond and Shdo 1966).

D.7.4.3.1 Flow and Heat Transport Calculations. Hydrologic parameters used in the simulations are those given in Khaleel et al. (2001). These flow and transport parameters represent effective (upscaled) values for the Hanford vadose zone and are broken out by the strata present at the S and SX tank farms (Table D.7.4.2).

Table D.7.4.2. Composite van Genuchten-Mualem Parameters for Various Strata at the S and SX Tank Farms (Khaleel et al. 2001).

Strata	Porosity	Residual Water Content	α (1/cm)	n	Vertical Ks (cm/s)	Horizontal Ks (cm/s)
Backfill	0.2688	0.0151	0.0197	1.4194	5.15E-04	5.15E-04
Fine sand (upper and lower)	0.3819	0.0443	0.0117	1.6162	9.88E-05	2.96E-04
Gravelly sand-sandy gravel	0.2126	0.0032	0.0141	1.3730	2.62E-04	7.86E-04
Plio-pleistocene	0.4349	0.0665	0.0085	1.8512	2.40E-04	7.20E-04
Sandy gravel	0.1380	0.0100	0.0210	1.3740	5.60E-04	1.68E-03

The distribution of permeabilities used in the simulations are shown in an X-Z section through tank SX-115 and 299-W23-19 borehole (Figure D.7.4.2). Except for the backfill, all of the strata are assumed to have horizontal conductivities 3 times their vertical conductivity. Based on the shape of cesium contamination detected in horizontal boreholes 10 feet below tank SX-115 (Raymond and Shdo 1966), the assumption of an anisotropy ratio of 3:1 appears to be reasonable. A larger anisotropy ratio would have spread the cesium contamination horizontally further than is observed if it can be assumed that the retardation of cesium is approximately the same in the horizontal and vertical directions. The tank is assumed to be impermeable. Boundary conditions

for the simulation consisted of no-flow boundaries on the side of the domain and fixed pressure boundary conditions at the bottom (the water table which is assumed to have a fixed depth) and the surface. A constant infiltration rate of 100 mm/yr is assumed at the top of the domain.

Figure D.7.4.2. Distribution of Permeabilities in an X-Z Section Through the Three-Dimensional Model Domain.

Note: See Table D.7.4.1 for the Various Hydrologic Parameters Used for Each of the Strata. The Upper and Lower Fine Sand Units are Assumed to have the Same Hydrologic Properties.

D.7.4.3.2 Chemical Initial and Boundary Conditions. Much of the point of the modeling exercise described here is to see how well various geochemical parameters taken from batch (Zachara et al. 2001; Section D.3.1) and column experiments (Carroll et al. 2001; Section D.3.3) can be used to describe the field transport of cesium and the other relevant cations. As discussed above, while sodium, calcium, magnesium, and potassium are not themselves significant contaminants, their behavior can be used to evaluate the field exchange capacity of the Hanford sediments. In addition, their behavior can be used as a partial test of the multicomponent ion exchange model. Accordingly, an effort was made to minimize calibration of the model so as to be able to evaluate directly the applicability of the experimental studies to the field.

The cation exchange capacities of the strata were assumed to be those determined by fitting of both batch and column experiments (Table D.7.4.1). While our best estimate of the actual CEC may change with further analysis (now under way), the key point is to use a combined set of CECs and selectivity coefficients that honor the column and batch experiments. With this

approach, we are in a good position to make a direct comparison of the laboratory and field cation exchange behavior. The initial composition of the exchangers is calculated by using aqueous concentrations of the cations that give the total masses of magnesium, calcium, and potassium eluted by flushing the Hanford sediment separately with NaNO_3 (reported in Carroll et al. 2001). Sodium could not be estimated easily because of the flush with NaNO_3 , but should be present in lower concentrations on the exchanger than any of the other cations.

The boundary condition at the top of the domain is assumed to be the same as the initial aqueous concentrations given in Table D.7.4.3. While rainwater will be considerably more dilute than these values, it is assumed that the infiltrating water evolves chemically before reaching the stratigraphic level of the Hanford sediments below the tanks. More important is the composition of the fluid leaking from the tank. Lichtner (2001) (Section D.7.3) has presented results based on reaction path modeling of the tank liquors using an approach similar to that employed by Jones et al. (2000). His results for tank SX-115 were used as a “base-case” for the simulations — a variety of runs were then carried out by diluting the “base-case” tank composition of Lichtner (2001). There is some anecdotal evidence at this point (not yet fully documented) that dilution of tank SX-115 did occur immediately before the 1965 leak and may actually have contributed to reopening an older leak.

Table D.7.4.3. Initial Aqueous and Exchange Compositions of the Hanford Sediment Estimated From Column Experiments and Simulations of Tank SX-115 Leak (field estimate).

Chemical component	Aqueous concentration (M)	Exchange concentration 5 M NaNO_3 column (eq/g)	Exchange concentration 1 M NaNO_3 column (eq/g)	Exchange concentration field estimate (eq/g)
PH	8.0			
HCO_3^-	5.70E-04			
NO_3^-	1.00E-06			
Ca^{++}	2.15E-03	8.43E-05	8.34E-05	7.09E-05
Na^+	1.00E-03			
K^+	1.94E-05	1.19E-05	4.8E-06	1.95E-05
Mg^{++}	5.00E-05	2.07E-05	1.78E-05	1.05E-05
Cl^-	6.31E-03			
SO_4^{--}	1.00E-05			
Cs^+	0.0			

D.7.4.3.3 Model Results-Flow and Temperature. Results presented here represent a preliminary attempt to verify that the ion exchange parameters determined from batch and column experiments can be combined with hydrologic parameters appropriate for the Hanford Formation to describe cesium, sodium, potassium, calcium, and magnesium reactive transport in Hanford sediments. Technetium and nitrate serve as nonreactive tracers that can be used to assess how well the flow regime is captured.

Simulated temperatures and liquid saturations (from NUFT) are shown at a point in time corresponding to the end of the 1-week leak event in 1965 (Figure D.7.4.3). Also shown are streamline plots of the flow field before and during the tank leak. The much discussed “umbrella effect,” where infiltration is funneled along the sides of the tank, shows up clearly in the closer spacing of streamlines along the tank edge. Both fluid velocity vectors and streamlines show the effect of the tank leak, with the enhancement in flow rates presumably due to the considerable weight of the fluid in the tank now allowed to penetrate into the vadose zone. The effect of the leak also appears in the temperature and liquid saturation fields.

Figure D.7.4.3. Temperatures, Liquid Saturations, and Streamlines Simulated by NUFT.

D.7.4.3.4 Model Results-Geochemistry. The simulated spatial distribution of the important chemical components associated with the tank SX-115 leak are shown in a series of X-Z sections cutting through tank SX-115 and 299-W23-19 borehole (Figure D.7.4.4). The results in the year 1999 predict that the nitrate (tracer) plume should have penetrated to a depth of 45 m below the ground surface. Na, in contrast, is noticeably retarded, with the leading edge of the plume occurring at about 39 to 40 m depth. The slightly elevated sodium values (in pale blue) above the main part of the aqueous Na plume is a zone in which sodium is concentrated on exchange

sites and is gradually being eluted by the infiltrating ambient rainwater/soil water. Since the infiltrating water is dilute, Na is only slowly eluted, and concentrations in the aqueous phase in this region remain low. Ca and Mg form well-defined plumes at the leading edge of the Na front. K forms a more diffuse plume that straddles the sodium and calcium plumes. Cs is predicted to be strongly retarded, with very little migration occurring beyond the site of the tank leak.

Figure D.7.4.4. Two-Dimensional X-Z Slice Through the Three-Dimensional Model Domain Corresponding to the Year 1999.

Note: The section cuts through both Tank SX-115 and Well 299-W23-19.

A direct comparison of aqueous geochemical data collected from the 299-W23-19 borehole and the simulations is shown in Figure D.7.4.5. The simulations capture quite closely the leading edge of all the exchange fronts, although the match with the trailing portions of the plumes is not as good. However, the simulations even capture some aspects of the complicated shape of the cation plumes, including the Na "shoulder" above the main part of the Na plume in the aqueous phase. This presumably represents Na being gradually eluted from exchange sites above the main zone of sodium in the aqueous phase. The simulated widths of the Mg, Ca and K plumes, are slightly too broad, although this may be the result of an overly coarse discretization. The relatively broader shape of the K plume, which shows up clearly in the data, is captured in an approximate fashion by the simulations. Cs, although not detected in significant amounts in the 299-W23-19 borehole, is known to occur very close to the bottom of tank SX-115 (see Figure D.7.4.3 and Raymond and Shdo 1966).

Figure D.7.4.5. Comparison of Three-Dimensional Simulation Results for the Tank **SX-115** Leak in 1999 and Geochemical Data for the 299-W23-19 Borehole.

Note: The simulation results do not include any calibration of the experimental (Batch and Column) CECs and ion exchange selectivity coefficients or the independently estimated hydrologic parameters.

It is important to point out that these results do not include any calibration of either the independently estimated hydrologic parameters (taken directly from Khaleel et al. 2001) or the laboratory-determined (batch and column) CECs and ion exchange selectivity coefficients. In order to match the absolute concentration of Na in the borehole, the composition of the tank leak fluid had to be adjusted (see Table D.7.4.4). The “best fit” value represents a dilution of the estimate provided by Lichtner (2001) (Section D.7.3) by about a factor of 3.5. To obtain a match in the absolute concentrations of Ca, Mg, and K, the initial exchanger compositions had to be adjusted from what they were determined to be in the column experiments (Table D.7.4.3). The “best fit” from matching the field data indicate a Ca exchange concentration quite close to that estimated from two of the column experiments (about 8×10^{-5} equivalents/g). The exchange concentration of magnesium determined in the column experiments, however, had to be adjusted downward by about a factor of 2 to obtain a match with the field data. Potassium had to be increased by factors ranging 2 to 4 over the values estimated from the column experiments.

**Table D.7.4.4. Composition of Tank SX-115
Leak Used in Simulations.**

Chemical Component	Base Case (M)	This Report (M)
PH	12.8	10.5
HCO ₃ ⁻	9.55E-03	2.70E-03
NO ₃ ⁻	1.19E+00	1.21
Ca ⁺⁺	5.30E-05	1.48E-05
Na ⁺	3.59E+00	1.30
K ⁺	1.10E-02	4.90E-03
Mg ⁺⁺	5.30E-05	2.37E-05
Cl ⁻	5.07E-02	1.43E-02
SO ₄ ⁻	1.92E-02	3.10E-03
cs+	8.25E-05	2.24E-05

D.7.4.4 Conclusions and Implications

Flow and reactive transport modeling of the tank SX-I 15 leak indicates that the ion exchange model developed by Zachara et al. (2001) and Carroll et al. (2001) provides an excellent basis for further field simulations of cesium transport. The column experiments provide more direct information on the effect of competing salt concentrations on Cs migration, but the field and modeling study carried out here is very valuable in establishing the effective field exchange capacity of the Hanford sediments. The well-defined chromatographic separation of the cations clearly demonstrates that the effective field CEC is close to the value determined independently in the batch and column experiments. Various hydrologic mechanisms for “bypassing” exchange sites (fast flow pathways or transport-limited sorption in immobile water zones), while not necessarily discounted altogether, do not appear to have had a large effect on the extent of cation exchange.

While there is still significant uncertainty with respect to the appropriate hydrogeologic parameters to be used in the flow and transport simulations, the chromatographic separation of cations that occurs below SX-115 provides a test of the applicability of the cation exchange model which, to some extent, does not depend entirely on knowing these parameters very accurately. This is because the chromatographic separation represents a relative separation of reactive cations and tracers. Whatever detailed flow field resulted in the present location of the tracer plumes, the observation that sodium and cesium are retarded relative to the tracers in the Z (depth) direction implies that the effective exchange capacity of the Hanford sediments had to be reasonably high.

It is likely that a similar exchange capacity applies below such tanks as tank SX-108 where Cs migration is much deeper into the vadose zone than it is at tank SX-115. Therefore, it would appear that the enhanced migration of cesium underneath tank SX-108 is chiefly the result of the very different chemical environment there, although the higher temperatures at tank SX-108 are likely to have produced a substantially different flow regime as well. In keeping with our observations from column experiments (summarized in Carroll et al. 2001), the much higher Na and Cs concentrations in the tank SX-108 leaks would contribute to a substantially lower retardation of Cs than would be expected at tank SX-115. At tank SX-108, for example, there is no retardation of Na relative to nitrate, which makes sense given the very high NaNO_3 concentrations there. If the extrapolation of the present ion exchange model and data to the NaNO_3 concentrations of SX-108 is valid, then a retardation of Cs that is as low as 2.5 or 3 can be explained by these high NaNO_3 concentrations. Other factors, however, are apparently operating at tank SX-108. Perhaps most important is the development of a "heat pipe" that draws flow into the boiling zone developed immediately below the tank. Preliminary simulations of the SX-108 leak indicate that the flow field is far from one-dimensional. During the boiling stage, fluid velocity vectors typically point up into the boiling zone. This "heat pipe" can lead to substantial accumulation of salts (especially NaNO_3) below the tank, due in part to the cooling of the fluid, but even more so to the dryout which results. This boiling zone, if it did result in substantial precipitation of salts immediately underneath the tanks, may have an important effect on Cs transport and needs to be carefully considered in assessments of the environmental impact of the tank leaks. While our work to date has shown that Cs will be largely immobile under dilute conditions, infiltration and rewetting of salts could lead again to high concentrations of such cations as Na and thus, potentially, to Cs remobilization.

D.7.4.5 References

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D.7.5 CONCLUSIONS OF S&T INVESTIGATIONS OF SIMULATION OF MULTIPHASE FLUID FLOW AND REACTIVE TRANSPORT AT THE SX TANK FARM

D.7.5.1 Nonisothermal Multiphase Fluid Flow

Radiolytic heating during the historical operation of the SX tank farm resulted in years of elevated tank temperatures (up to 200 °C). These temperatures were sufficiently high to significantly alter fluid distribution in the sediments surrounding the tanks. Two sets of modeling analyses, (1) axially symmetric single tank and (2) two-dimensional vertical cross-section multitank, were performed to determine the impact of the tank heat sources on fluid migration by comparing nonisothermal and isothermal modeling results. The hydrologic conceptual model is based on descriptions provided by the River Protection Project (RPP) and will be tested against field observations of temperature and moisture content. Understanding the impact of the heat-induced fluid migration is important when considering travel time of the existing contaminant inventory, and is especially germane in the context of recently measured temperatures in the sediments beneath tank SX-108 that exceed 70 °C. This is a critical consideration for decisions on surface barrier construction and limits on leak loss during tank waste retrieval operations.

Key Findings

- In the SX tank farm vadose zone, tank heat sources have a large impact on liquid saturation and fluxes. In sediments adjacent to these high-heat tanks, pore fluid evaporates into water vapor that is driven away to locations where lower temperatures result in condensation. As the sediments adjacent to the tank dry out, strong capillary forces are induced, drawing more pore fluid to this zone. This liquid-vapor counterflow is predicted to be most significant in the sediments just below the tank bottom (where the tank temperatures are highest) resulting in sediments that are essentially dry.
- When tank temperatures decrease, evaporation decreases; however, capillary forces are still sufficient to draw pore fluids to the dried sediments, rapidly rewetting the sediments. During operational fluctuations in temperature within a tank or between tanks, significant rewetting is predicted to occur over periods as short as a few months.
- In the zone where this liquid-vapor counterflow (also known as the heat pipe effect) is occurring, pore fluids from surrounding sediments are continuously drawn in while water vapor is continuously driven away, allowing salts to accumulate. In particular, highly concentrated sodium solutions as well as the precipitation of sodium minerals are predicted to occur in the sediments adjacent to the high heat tanks. This is a significant finding because very high concentrations of free sodium can substantially reduce cesium sorption, thus causing Cs-137 to migrate with minimal retardation. Furthermore, future rewetting of precipitated sodium salts from natural or artificial recharge could result in sodium concentrations sufficiently high to remobilize previously sorbed cesium.
- The sloping gravel layer in the Hanford formation provides a path away from SX-108 towards SX-109 for fluid migration (natural and heat induced). This underscores the

importance of accurately characterizing the geometry and hydrologic parameters of the vadose zone sediments in the SX tank farm.

- **An** effective surface barrier can significantly control transport to the water table driven by recharge. Timing of the construction is critical as earlier construction will increase travel times, which increases opportunities for mixing, which effectively reduces peak concentrations.

D.7.5.2 Speciation of High-Ionic Strength Tank Fluids

A critical modeling data need is a reasonably representative composition and speciation of the *tank* fluids at the time of the leaks. The characterized *tank* fluid species and concentrations are fundamental to the reactive behavior that takes place in the vadose zone sediments. They are complicated by *tank* fluid that was historically high in temperature (~110 °C) with highly concentrated electrolytes. Significant differences in reactivity and solubility occur at these temperatures compared with thermodynamics at 25 °C. Standard Debye-Huckel activity corrections are inaccurate at these concentrations and ion-specific treatment (e.g., Pitzer ion interaction parameters) is necessary to account for non-ideal, high-ionic strength effects on reactivity. An important requirement under these conditions is the explicit accounting for water as a species since the solution may be less than 70% water.

Very few historical analytical measurements of *tank* fluids have been identified. Consequently, the principal source of *tank* fluid composition is from estimates based on process waste stream records, *tank* transfers, and evaporative losses [e.g., Hanford Defense Waste (HDW) Model]. The objective of these analyses is to examine assumptions underlying the tank fluid speciation calculation, especially as they relate to source term concentrations of critically important chemical components. The analyses specifically address temperature, ionic strength, and mineral precipitation. The resulting speciation of the tank source terms has significant implications for the mobility of some contaminants (e.g., cesium).

Key Findings

- Using tank compositions from the HDW Model as a starting point, charge balancing with OH⁻ results in higher pH and sodium concentrations as compared to the speciation performed by Jones (2000). At high temperature and ionic strength, the predicted SX-108 free sodium concentrations are sufficiently high to significantly reduce the retardation of cesium in the sediments.
- Mineral solubility exerts significant control over the speciation of the tank fluids. This underscores the importance of correctly identifying the actual mineral phases present in the tanks.

D.7.5.3 Cesium Migration Beneath Hanford Waste Tanks

Mobility of cesium-137 was the galvanizing issue behind the current focus on the Hanford Site Vadose Zone. Considerable resources have been directed at elucidating the process mechanisms that can account for observations of cesium-137 at depth in the SX tank farm. The objective of this analysis is to test the understanding of cesium-137 developed from these studies, in the

context of the field situation at SX-108 and SX-115. This can be problematic given the uncertainties in tank leak volumes, rates, and composition, as well as the fact that total cesium can be 4 to 5 times the Cs-137 concentration. However, the tank leak at SX-115 in 1965 was unique because the leak volume (50,000 gallons) and duration (1 week) are constrained by direct observations. At the time of the leak, SX-115 was not a high temperature tank. Coupled with a comprehensive data set from the recently characterized well, W23-19, SX-115 was ~~the~~ logical starting point for modeling cesium migration in a multicomponent reactive system ~~that~~ accounts for competitive cation exchange. The SX-115 analysis provided the basis for the subsequent modeling of cesium migration beneath SX-108.

The analysis of the SX-115 leak was carried out by combining the multisite cation exchange model with modeling of 3D flow and transport using the Hanford hydrostratigraphy and hydrologic parameters as presently known. Although there is little direct interest in sodium, calcium, magnesium, and potassium as contaminants, these cations are very useful in establishing whether the multicomponent ion exchange model developed to describe cesium exchange and transport in the batch and column experiments can be applied to the field. The ability to match the chromatographic pattern of the cations other than cesium provides a test of the self-consistency of the multisite cation exchange.

Key Findings

- Component concentrations in the tank source term developed from the HDW model appear to be consistently **high** with respect to our interpretation of the leak event and the chemical analyses of the borehole samples.
- After developing a “best fit” dilution of the HDW estimated source term, the multisite cation exchange model developed from laboratory studies provided a reasonable match with the entire suite of cations (cesium, sodium, calcium, potassium, and magnesium) at SX-115. This consistency between field observations and predictions based on laboratory derived cation exchange capacities (CECs) and selectivity coefficients lends strong support for the cation exchange model developed to describe cesium migration at Hanford.
- The analysis suggests that fast pathways and bypassing of immobile zones due to low saturation conditions are unlikely to explain the major chromatographic patterns observed below the leaking SX tank farm.

D.7.5.4 Identification of Critical Data Needs

In the course of these model-building activities, gaps in knowledge and data were identified as well as the applicability of simplifying assumptions. Issues that have been identified:

- **Hydrologic characterization parameters** – At this point in time, no sediments from the SX tank farm have been characterized for soil moisture retention functions. Current parameterizations are based on historical studies of sediments from areas other than the SX tank farm and little effort has been made to adjust these parameterizations in light of the field observations of moisture content. Permeability anisotropy has been shown to

significantly impact fluid migration in field experiments; however, mechanistic parameterizations have not been characterized.

- **Tank leaks** – Fluid migration in the Hanford Vadose Zone is sensitive to the rate and duration of recharge (natural and artificial). Unless tank leak rates were very high, it was difficult for them to be detected other than through gamma logging for cesium in the laterals. SX-108 is an example where a chronic, but not obvious leak was probably occurring through the high heat operations in the 1960s. Leak estimates at SX-108 have ranged from a few thousand gallons to over 200,000 gallons based on a variety of estimation approaches.
- **Tank fluid speciation** – Speciation of the tank fluid at the time of the leaks will ultimately dictate the behavior of contaminants that chemically interact with the sediments. Differences in high-ionic strength thermodynamic models and databases need to be understood and updated to achieve consistency in the characterization of the source term being introduced into the sediments.
- **Field and laboratory experiments** – The lack of information on tank composition and speciation is a surprisingly common theme considering the amount of ongoing research that is depending on it. Experimental studies of tank chemistry under high temperature conditions, including the formation of secondary minerals, would provide some needed constraints on the speciation conceptual model.

D7.5.5 Next Steps

We consider the analyses presented here to be a preliminary step in identifying where additional detail and complexity are needed to assess the appropriate representation of subsurface processes in predictive models of the Hanford Vadose Zone. Subsequent modeling analyses will focus on:

- Three-dimensional, multitank simulations to more realistically identify the impact of multiple tanks and their temperature histories on fluid and contaminant migration to the water table and beyond.
- Developing new estimates of tank leak volumes and rates based on the systematic comparison with observed chemical concentrations, moisture contents and temperatures.
- Linkage of the full multicomponent reactive chemistry system to nonisothermal multiphase fluid flow to determine the potential for highly concentrated salts beneath the tank bottom which could result in cesium mobility during rewetting.
- The reactivity of mineral surfaces exposed to the extreme physical and chemical conditions of the tank fluids.
- Chromium interaction with Fe^{++} released by the dissolution of minerals from the interaction of tank fluid with vadose zone sediments.

D.8.0 VADOSE ZONE FIELD EXPERIMENTS AND INFILTRATION ESTIMATES FOR THE S AND SX TANK FARMS

Tank waste contaminants such as chromate, nitrate, technetium, and tritium, among others, continue to be found in increasing concentrations in groundwaters beneath tank farms and burial grounds at the Hanford Site (e.g., 618-11). Cores collected from beneath leaked tanks in the S and SX tank farms, and others, display complex solute concentration profiles indicative of highly anisotropic hydrologic processes. Vadose zone contaminant distributions in one borehole, often seem in conflict with those from another nearby borehole, or groundwaters that are vertically below. These observations all suggest that water movement through the Hanford vadose zone, and the factors that control it are poorly understood. There is an urgent need for: (1) more information about the transport of contaminants as they move through the vadose zone to the underlying water table, and (2) improved models of water and solute migration with appropriate scale dependencies.

A critical information requirement in assessing the need for corrective actions in the S and SX tank farms is the infiltration rate of meteoric waters. It is well known that the infiltration over vegetated soils near the tank farms increased after the native vegetation was removed from the tank farms and the area was covered by over a meter of gravel. The modeling assessments presented in the body of the report assumed an infiltration rate (100 m d yr [4 in./yr]) as the basis of their calculations. But, are these rates reasonable? The infiltration rate controls the timing of solute breakthrough from the vadose zone to groundwater. Surface barriers, that reduce the infiltration rate, are one of the most logical corrective actions that could be applied in the tank farms. Credible estimates of recharge are therefore needed for the S and SX tank farms and others in order to estimate travel times to groundwater and the remedial contributions of barriers.

In this Appendix section, we describe hydrologic studies that have been performed in support of the WMA S-SX field investigation. These studies include: (1) field injection experiments at the vadose zone test facility (VZTF) designed to evaluate the influence of fine-textured sediment layers on water movement, and (2) infiltration estimates at the S and SX tank farms using a water-balance approach calibrated against Hanford lysimetry data.

D.8.1 HANFORD VADOSE ZONE TRANSPORT FIELD STUDIES

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D.8.1.1 Introduction

The scope of the Vadose Zone Transport Field Studies (VZTFS) is to conduct a series of tests at the Hanford Site to evaluate how contaminant plumes move in the vadose zone. This information will be used to improve predictions of vadose zone contaminant transport at *tank* farms and other waste disposal sites. A series of flow and transport experiments at uncontaminated sites focused on characterizing transport processes and parameters in the Hanford subsurface and generating accurate and reliable databases for testing three-dimensional numerical vadose zone models of flow and transport. The VZTFS plan calls for conducting two flow and transport tests at an uncontaminated site to simulate a near-surface tank leak, followed by two flow and transport tests in deeper Hanford formation sediments. During FY 2000, the first of four field tests was completed using a low ionic strength solution (1000 ppm).

The objectives of the VZTFS are to conduct controlled transport experiments at well-instrumented field sites at Hanford to: (1) identify mechanisms controlling transport processes in soils typical of the hydrogeologic conditions of Hanford's waste disposal sites, (2) reduce uncertainty in conceptual models, (3) develop a detailed and accurate database of hydraulic and transport parameters for validation of three-dimensional numerical models, and (4) identify and evaluate advanced, cost-effective characterization methods with the potential to assess changing conditions in the vadose zone, particularly as surrogates of currently undetectable high-risk contaminants.

A detailed test plan (Ward and Gee 2000) outlines the overall scope of the VZTFS. Activities focus on hydrogeologic investigation and characterization of field sites to address current data gaps in transport of mobile contaminants by making in situ measurements of surrogate parameters using new monitoring technologies.

D.8.1.2 Experimental Approach and Methods

Testing has been approached in two phases: (1) characterization of background site conditions, and (2) process characterization that will occur during and after the actual transport test and will include assessment of the physical and chemical properties affecting the vadose zone transport processes.

A test location was selected at Hanford in the 200 East Area (299-E24-111, also referred to as the Sisson and Lu Site), where an extensive amount of characterization had already been completed (Sisson and Lu 1984; and Fayer et al. 1993, 1995). Ward and Gee (2000) provide details of the site selection process. Figure D.8.1.1 shows the site location.

Figure D.8.1.1. Location of Sisson and Lu Test Site.

Note: The Site is designated as 299-E24-111, experimental Test Well Site in the Hanford Waste Information Data System (WIDS).

The geology at the test site is well characterized. The surface soil at the site is a coarse sand, locally known as a Quincy sand, which is associated with the Quincy soil series. The soil has a high infiltration capacity (greater than 50 mm/h [2 in./hr]) and precipitation infiltrates readily with little or no runoff. The vegetation at the site before the experiment was a mixture of sagebrush and cheatgrass. The shrubs on the site were "grubbed" off in March 1980 and since that time the site has been dominated with a sparse cover of cheatgrass, tumble mustard, and tumbleweed (Fayer et al. 1993). Below the surface soil is the Hanford formation, which extends to about 60 m (200 ft) below the surface. The water table is more than 90 m (295 ft) deep. Therefore, the field injection experiment was conducted in the Hanford formation sediments.

The original field experiment (Sisson and Lu 1984) consisted of a central injection well surrounded by 32 observation wells. The wells are constructed of 15.24-cm (6-in.) diameter steel casing and extend to 18 m (59 ft). The FY 2000 field test included a series of new boreholes and instruments installed by auger and cone penetrometer. A new injection well was installed at the site and vertical electrical resistance tomography (ERT) arrays were employed by

cone penetrometer. The layout of the FY 2000 field test is illustrated in Figure D.8.1.2, showing a plan view of the locations of access tubes, electrode arrays, and injection and core sampling points.

Figure D.8.1.2. Plan View of FY 2000 Test Site Showing Locations of Access Tubes, Vertical Electrode Arrays, Injection, and Core Sampling Points.

More than 20 technologies were screened to identify those that could be used to delineate the moisture and contaminant plume during the field injection tests, either as stand alone technologies or used in conjunction with others. With this objective in mind, a short list of candidate technologies was identified based on the following criteria which included the ability to (1) identify key geologic features controlling water movement with a vertical resolution of 0.1 m (4 in.) or better and a horizontal resolution of 1 m (3.3 ft) or better, (2) locate wetting fronts and a change in water content of $0.01 \text{ m}^3/\text{m}^3$ or better with a repeatability of at least $0.01 \text{ m}^3/\text{m}^3$, (3) determine the shape and extent of non-gamma-emitting contaminant plumes or their surrogates, and (4) function and produce useful results in environments that are culturally noisy.

The nine technologies selected from the screening process included neutron moisture logging, advanced tensiometry/suction lysimetry; electrical resistance tomography (ERT); crosshole radar tomography (CRT); crosshole seismic tomography; crosshole electromagnetic induction (CEMI); and high-resolution resistivity (HRR). Additional methods included tracers (including isotopes), and coring. The details of each of the nine methods selected and the collaborators who helped deploy the selected methods are listed in the VZTFS test plan (Ward and Gee 2000).

For the FY 2000 study, water content changes were the primary measurement variable. Water content as determined by neutron probe logging was selected as the primary standard upon which the other geophysical methods could be compared. Neutron probes were used in the past to monitor water content at the Sisson and Lu injection site (Sisson and Lu 1984; Fayer et al. 1993 1995). These probes are also used routinely to monitor field water contents at the Hanford Site. Details of the calibration of neutron probes for monitoring water content at the Sisson and Lu site are provided by Fayer et al. (1995).

D.8.1.3 Field Tests and Results

In late April 2000 the site was approved for use and installation of equipment (e.g., electrodes for electrical resistance tomography, cross-borehole ports, and advanced tensiometers) began in early May. Electrode, port, and tensiometer placements were completed before scheduled baseline measurements by all of the geophysical methods before starting water injections.

A total of nine methods were tested: neutron probe logging, electrical resistance tomography (ERT), cross-borehole radar (XBR), seismic (XBS), high-resolution resistivity (HRR), electromagnetic imaging (EMI), and advanced tensiometry (AT). In addition isotopic tracers were deployed during the test and subsequently sampled by soil coring. Soil coring was also used to obtain samples for hydraulic characterization. A schedule was established so that baseline sampling and subsequent data collection from each method could be obtained in the most efficient manner and so that there was minimal interference between methods. For example, XBR and ERT measurement schedules were compatible and these measurements could be made simultaneously with the neutron probe. In contrast, the HRR and EMI measurements could not be taken at the same time so a rather strict schedule was set to ensure collection of the best possible data. Table D.8.1.1 shows the detailed schedule for the FY 2000 test.

After baseline data from all methods were obtained, a series of 5 injections were performed, beginning on June 1, 2000, when 4000 L (1060 gal) of water was metered into the 5-m (16.4-ft) deep injection well over a 6-hour period. Subsequent injections occurred weekly for a period of 5 weeks. The third injection included 1000 ppm bromide and a suite of isotopic tracers. Neutron logging of 32 steel-cased wells (surrounding the injection well) occurred before the initial injection and followed each of the 5 injections within a day, with the exception of the injection that occurred on June 26, 2000. On that day a wildfire burned within about 0.5 km (0.3 mi) of the test site. After the injection, the Hanford Site was closed to traffic due to the fire, so no neutron logging occurred at the test site July 7. Subsequently two more readings of the 32 wells were completed during the month of July. One additional 4000 L (1060 gal) injection was made on September 18. This injection was made to obtain in situ hydrologic properties using a combination of pressure measurements and neutron probe water content measurements at the same depth. Only limited water content measurements were made at a few selected locations

and no other geophysical measurements were made after the September injection. Details of the neutron-probe logging are provided in a companion report (Ward and Caldwell 2000).

Water content profiles measured by neutron probe (Figure D.8.1.3) captured the nature of the plume during the course of the injection testing and indicated that water content changes below the 11-m (36-ft) depth were minimal, suggesting that the plume spread laterally along layers of finer sediments which were noted at 6 and 11 m (19.7 ft and 36 ft). The FY 2000 test was simulated using STOMP, a multiphase (unsaturated) flow and transport code developed at PNNL. Conditional simulation of the five injections was made using methods developed by Rockhold et al. (1999). The simulations were conditioned on the initial water contents and the water retention characteristics of Hanford Site soils that are similar but not identical to those soils found at the Sisson and Lu site.

Figure D.8.1.3. Two-Dimensional Cross-Sections of the Water Content Profile Measured by Neutron Probe after Four Injections on June 23, 2000.

Note: Figures a), b), c) and d) represent cross-sections taken along transects EA, DH, CG and BF, respectively (see Figure D.8.1.2).

Table D.8.1.1. List of FY 2000 Test Activities for the VZTFS project at the 299-E24-111 Experimental Test Well (Sisson and Lu) Site, 200 E Area, Hanford Site, Washington. (2 Sheets)

Date	Action	Method 1	Method 2	Method 3	Method 4	Method 5	Method 6	Method 7	Method 8	Method 9
03-May	Pre- Leak	Neutron	AT Tens.	ERT	XB Radar	Seismic	EMI	HRR	Isotopes	Coring
05-May 06-May	Pre-	Read 35								
06-May 09-May		Cross-Calibrate								
09-May				CPT Install (3 day)						
12-May			CPT Install (2 day)							
15-May					CPT Install (2 day)					
19-May										Install/ Inject
20-May			Install Nest (2 day)				Set up/ Read (3 day)			
23-May			Read- continuou sly	Setup/ Read (3 day)						
25-May					Set/Read					
26-May					Read			Set/Read		
30-May								Read	Sample	Core (S-1)
31-May								Read	Samples	Core (S-1)
01-Jun	1 st Leak			Read						
02-Jun		Read 32		Read						
05-Jun							Read (2 day)			
08-Jun	2 nd ak	Lead 8								
09-Jun		Lead24								
12-Jun										
13-Jun					Read					
14-Jun				Read	Read					
15-Jun	3 rd Leak	Lead 8		Read						
16-Jun		Lead24		Read						

Table D8.1.1. List of FY 2000 Test Activities for the VZTFS project at the 299-E24-111 Experimental Test Well (Sisson and Lu) Site, 200 E Area, Hanford Site, Washington. (2 Sheets)

Date	Action	Method 1	Method 2	Method 3	Method 4	Method 5	Method 6	Method 7	Method 8	Method 9
		Neutron	AT Tens.	ERT	XB Radar	Seismic	EMI	HRR	Isotopes	Coring
19-Jun								Read (6 day)		
21-Jun										
22-Jun	th Leak	Read 8								
23-Jun		Read 24								
24-Jun										
28-Jun	th Leak	Read 8/Fire			Read					
06-Jul									Samples	Core (S-2)
07-Jul	ost eak	Read 32			Read (2 day)				Samples	Core (S-2)
10-Jul				Read (2 day)					Samples	Core (S-3)
13-Jul							Read (2 day)			
14-Jul							Read			
17-Jul		Read 32								
21-Jul									Samples	CPT (WL1)
31-Jul		Read 32								
1-Aug						Read (2 day)				
11-Sep									Samples	CPT (WL2)
12-Sep									Samples	CPT (WL2)
15-Sep			CPT (2 ATs)							
18-Sep	ulse	Read (5 day)	Read (5 day)							

The results indicate that the model captures the general flow depths and directions of the plume but does not completely describe the extent of the lateral spreading of the plume. Hydraulic property data collected during the testing this past year may be helpful in improving the prediction of the lateral spreading. These estimates will be updated in FY 2001.

D.8.1.4 Conclusions and Implications

The first of two field tests at the 299-E24-111 (Sisson and Lu 1984) injection site in the 200 East Area of the Hanford Site was completed during FY 2000. The results of the injection experiments indicate that lateral **flow** appears to dominate much of the transport that occurs in Hanford sediments. Sediment layering, even subtle changes in texture can do much to cause lateral spreading of water and contaminants. The observed lateral movement of cesium near tank SX-109 (Price and Randall 1998) may be caused by lithologic control of the hydraulic properties.

All of the geophysical methods deployed in the field experiment were successful to some degree in identifying changes in subsurface water contents (or pressures) as a result of the five injections. Work in FY 2001 is focused on using the most successful geophysical techniques and isotopic tracers. During the FY 2001 field experiment, a high salt concentration (>1M) will be added in the water injections and the salt plume is being tracked with geophysical logging and solution sampling techniques similar to those used in FY 2000.

Summary reports for the FY 2000 tests can be found at the following Universal Resource Locator (URL) address: <http://etd.pnl.gov:2080/vadose/contrpts.htm>. Analysis of the data is continuing through FY 2001 and a final report describing the FY 2000/2001 testing will be published in September 2001.

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D.8.2 ESTIMATION OF NET INFILTRATION OF METEORIC WATER AT THE SX TANK FARM

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D.8.2.1 Introduction

There is mounting evidence that mobile constituents (e.g., ^{99}Tc , chromate, and nitrate) from tank leaks have reached groundwater (Serne et al. 1997; Johnson and Chou 1998; Hodges 1998; Narbutovskih 1998; Myers et al. 1998) at Hanford Site tank farms. One cause for the transport of mobile constituents to groundwater is deep infiltration of winter rains and episodic snowmelt runoff that leach soil contamination from the vadose zone to the underlying water table.

The accelerated movement of water around and beneath buried tanks can be attributed to bare, gravel surfaces that enhance net infiltration of meteoric water (from winter precipitation and snow melt) (Smoot et al. 1989; Connelly et al. 1992; Ward et al. 1997). The FIR provides insights into mechanisms that control the migration rates of contaminants that leak from tanks into groundwater at the SX tank farm. These observations can be used to assist in mitigating leaks both now and in the future, when tank sluicing and other operations may require additions of water to ruptured or otherwise leaking tanks or to transfer lines. Interest in net infiltration (drainage) rates stems from the assumption that contaminant plumes are largely driven by advective water flowing in the subsurface, gravity drainage being the dominant mechanism for transport of mobile contaminants in the vadose zone.

Simplified calculations, assuming a conservative scenario for transport (e.g., one-dimensional vertical transport of nonreactive contaminants moving through coarse, highly permeable sediments) can be used to illustrate the problem. Assume that a tank leak occurred in 1970 from a tank whose bottom was **60 m (200 ft)** from the water table. Typical water contents in coarse Hanford sediments under draining conditions are 7% by volume or less. If the average flux of water around the tank and impacting the tank leak is 70 mm/yr (2.8 in./yr), then the contaminant transport rate for a leak beneath the tank is 1 m/yr (3.3 ft/yr). Thus, in 60 years, the contamination from the tank leak will reach the water table. Under tank farm conditions, the buried tanks create concentrated flow paths adjacent to the tank walls, so pore-water velocities can locally exceed 1 m/yr (3.3 ft/yr), accelerating the flow and reducing the travel time to the water table. If concentrated flow pathways exist or localized recharge zones have developed at some point in the tank farm, the recharge rates can also be accelerated. Support for localized recharge zones have been documented in recent tank farm reports (Hodges 1998; Johnson and Chou 1998; Narbutovskih 1998). While it may be difficult to obtain detailed data on localized flow around tanks, it should be possible to obtain estimates of the net infiltration into a tank farm. For tank farms, we define the net infiltration as synonymous with drainage and equivalent to precipitation minus evaporation. This net infiltration (drainage) then becomes the driving force for most, if not all, of the contaminant migration that occurs at the tank farm. The following analysis is used to estimate drainage rates at the SX tank farm and to predict future drainage rates, assuming that the surface cover does not change substantially until final closure.

D.8.2.2 Water-Balance Analysis

Deep drainage at tank farms and other Hanford waste sites is best analyzed by assessing the complete water balance of the surface soils. Drainage is an integral component of the water balance, which in its simplest form can be written as:

$$D = P - S - ET - RO \quad (D.8.2.1)$$

where:

D = drainage

P = precipitation input

S = storage change

ET = evapotranspiration

RO = runoff/run-on.

Three main variables, climate, soils, and vegetation, control the water balance of surface soils. The assessment of net infiltration (drainage) at the tank farms involves the interaction of these three factors. Topography also can affect drainage due to runoff or run-on, but most tank farms are on relatively level ground or are bermed so that runoff or run-on are controlled or minimized.

D.8.2.2.1 Climate. The Hanford Site can be characterized as arid, the dominant climatic features being cool, wet winters coupled with hot, dry summers (Stone et al. 1983; Rickard et al. 1988). While there are no site-specific, long-term weather records for individual tank farms, a reliable source of meteorological data (e.g., precipitation, wind speed, air temperature, humidity, solar radiation) is the Hanford Meteorological Station (HMS), located on the 200 Area plateau between the 200 East and 200 West Areas and within a few kilometers of all of the tank farms. The HMS records have been kept since the late 1940s and thus cover the time period of interest for all tank farm and other 200 Area waste site operations at Hanford. For the past 20 years, precipitation has averaged 184 mm/yr (7.2 in./yr), about 14% above the historical average (Hoitink et al. 2000). During this time, annual precipitation amounts have varied by more than a factor of three, ranging from a record high of 313 mm/yr (12.3 in./yr) in 1995 to a low of 95 mm (3.7 in.) in 1999. While variations in both seasonal and annual precipitation strongly affect drainage rates at the tank farms, the most dominant factor appears to be winter (November through March) precipitation. Winter precipitation during the past 20 years at Hanford has varied from a record high of 224 mm (8.8 in.) in 1997 to a low of 58 mm (2.3 in.) in 1990. Winter months typically have the greatest amount of precipitation (over 62% of the annual average) and the lowest amount of evaporation. Precipitation occurring outside of the winter period appears to contribute little to drainage (Gee et al. 1992; Fayer et al. 1999).

D.8.2.2.2 Soils. All tank farm surfaces consist of coarse-textured backfill materials. At some tank farms (e.g., BY, BX), commercial "top-course" materials (gravelly sands) have been added to cover surface contamination and provide operational stability for worker access. These well-drained sediments hold little water, transmitting it readily to the underlying sediment of the Hanford formation (Tallman et al. 1979). There is very limited characterization data on surface soils at tank farms, but some textural information is available (Smoot et al. 1989). More detailed soil characterization, such as saturated and unsaturated hydraulic conductivity, particle-size

analysis, and water-retention characteristics of surface sediments, would be helpful in future assessments of the tank farms.

D.8.2.2.3 Vegetation. All tank-farm surfaces are kept vegetation free. Plants are kept off tank-farm surfaces by application of herbicides and soil sterilants. The control of vegetation is important in the tank **farm** operations because of concerns about radiation uptake by plants (e.g., radioactive tumbleweeds). Without vegetation, there is no root zone for plant water uptake, and evaporation is the sole mechanism for upward removal of water. In coarse soils, the lack of vegetation greatly increases the potential for drainage.

D.8.2.2.4 Tank Farm Water Balance. Based on the above description of climate, soils, and vegetation, we developed a simple water-balance model for surface soils at the Hanford Site tank farms. The model assumes the following conditions for the tank farms.

- (1) Winter precipitation dominates the net infiltration process.
- (2) Water runoff and run-on at tank farms are negligible.
- (3) Annual water-storage changes are negligible.
- (4) Soil texture (e.g., particle-size distribution) controls the amount of water retained in the surface and influences the overall evaporation rate.
- (5) The soil surface remains unvegetated (upward water movement is by evaporation only [i.e., no transpiration or water uptake by plants]).

Based on the above assumptions, the surface-water balance can be written **as**:

$$D = (P_1 + P_2) - (E_1 + E_2) \quad (\text{D.8.2.2})$$

where

P_1 = winter (November through March) precipitation
 P_2 = Non-winter (April through October) precipitation
 E_1 = winter evaporation
 E_2 = Non-winter evaporation.

Combining terms leads to the following expression:

$$D = P_1 - E_f \quad (\text{D.8.2.3})$$

where $E_f = (E_1 + E_2) - P_2$ is an evaporation factor.

E_f is dependent upon soil texture and precipitation. Based on an analysis of lysimeter records (Gee et al. 1992; Fayer et al. 1999), we determined the impact of precipitation and soil texture on drainage for a range of surface conditions, ranging from clean, washed gravels to fine-textured silt-loam soils. The following relationship was developed:

$$E_f = E_f^0 \text{ for } P_1 > 80 \text{ mm/yr} \quad (\text{D.8.2.4})$$

$$E_f = E_f^o [P_1/115]^{0.5}, \text{ for } P_1 \leq 80 \text{ mm/yr} \quad (\text{D.8.2.5})$$

where $E_f^o = 0.0069 f^3 - 0.43 f^2 + 12.64 f + 25.157$ with f being the % fines (all material less than 53 microns in size).

The performance of this model is shown in Figure D.8.2.1, where the model is applied to a PNNL lysimeter located just north of the 300 Area at the Hanford Site. The PNNL lysimeter has a bare sand surface, is 8 m (26 ft) deep, and has been draining for the past 20 years (Gee 1987; Gee et al. 1992; Tyler et al. 1999). The agreement between modeled and observed drainage is reasonable. It must be kept in mind that the model was not independent of the lysimeter data because the total drainage from the lysimeter was used in fitting the evaporation factor, E_f , for coarse sand. The model was then applied to independent data from the Hanford Solid Waste Landfill (SWL) lysimeter (DynCorp 2000). The SWL lysimeter is a 7-m (23-ft) deep, basin-type lysimeter with a capture area of 85 m². Figure D.8.2.2 indicates that drainage has occurred from the SWL landfill since July 1996 (the lysimeter was placed at the bottom of the landfill trench in 1992 and subsequently filled over the next 3 years). Drainage has been collected from this site since July 1996 (DynCorp 2000). Cumulative drainage has been 280 mm (11 in.), averaging 62 mm/yr (2.4 in./yr). Table D.8.2.1 shows the measured annual drainage compared to that predicted by the water-balance model for a 4-year period (i.e., Equation D.8.2.3). It should be noted that **annual** drainage is predicted within 4 mm (0.16 in.) for all 4 years. *Also* note that for the calendar year 1997, the winter precipitation of 224 mm (8.8 in.) exceeds the 1997 annual value of 162 mm (6.4 in.). This results from the calculation of winter precipitation (November 1996 through March 1997), which includes a record 162 mm (6.4 in.) from November and December 1996. Fortunately, the November through December record precipitation is identical to the entire 1997 annual value, illustrating the extreme variability in Hanford climate. The wide variation in the ratio of drainage to total precipitation (last column) reflects the importance of precipitation distribution and supports the concept that winter precipitation and soil texture are more important than total precipitation in determining drainage rates for bare waste sites at Hanford.

Figure D.8.2.1. Twenty-Year Record of Measured and Predicted Drainage From PNNL Lysimeter.

Note: The lysimeter is an 8-m (26 ft) deep and sand filled. The lysimeter are part of a tank farm water balance model. The model uses the Met Office (Met Office Station) climate record and the soil texture (3% fines).

Figure D.8.2.2. Solid-Waste Landfill Drainage at the Hanford Site.

Note: The landfill was closed in 1995 and drainage began in July 1996. The Lysimeter is located below the landfill at a depth of 7 m (23 ft).

Table D.8.2.1. Measured Drainage at the Hanford Solid Waste Landfill Compared to that Predicted by Tank Farm Water Balance Model.

Year	Annual Precipitation (mm)	Winter Precipitation (mm)	Measured Drainage (mm)	Predicted Drainage (mm)	Drainage as % Total Precipitation
1997	162	224	162	158	100
1998	164	107	41	42	25
1999	95	86	22	21	23
2000	20s	88	19	23	9

Note that in 1997, the winter precipitation exceeds the annual. This is a result of the differing time period for the two precipitation amounts and the record winter precipitation (November 1996 through March 1997). Uncertainty in the drainage is dependent on uncertainties in the surface texture. Variations in texture (percentage of fines of several percentage points can alter the drainage estimate by 10 to 20 mm/yr (0.4 to 0.8 in./yr) or more, particularly when the percentage of fines is low (less than 10). It should also be noted that modest increases in the percentage of fines significantly reduces the drainage. An increase of percent fines from 1 to 7 % reduces the predicted drainage by a factor of nearly three, from 80 to 28 mm/yr (3.1 to 1.1 in./yr). Based on modeling results, Smoot et al. (1989) suggested that adding silt-loam soils to tank-farm surfaces was one means of virtually eliminating net infiltration (drainage).

D.8.2.2.5 Model Predictions. Drainage predictions were developed for several tank farms where textural data were available for surface sediments. Table D.8.2.2 shows the predicted annual drainage, based on surface texture and the past 20-year-climate record. No soil-texture data are currently available for surface sediments of SX tank farm. Assuming that the SX tank farm has a surface texture similar to S tank farm, the estimated average drainage rate for the SX tank farm is 56 mm/yr (2.2 in./yr).

Table D.8.2.2. Predicted Tank Farm Drainage Rates Related to Percent Fines in Surface Sediments and Percentage of Annual Precipitation Based on 20-Year Record.

Site/Soil	% Fines	Drainage (mm.yr)	% Precipitation
AP tank farm	1	80	43
S tank farm	3	56	30
U tank farm	7	28	15
Coarse Gravel	0	98	53
SWL Site	3	56	32
Silt Loam	60	0	0

D.8.2.3 Discussion

Data available from lysimeter studies at Hanford have shown that winter precipitation and surface textures are the dominant controls to waste-site drainage. The calibration data set contained the past 20-year-precipitation record and drainage from lysimeters with surfaces ranging from clean gravels to fine silt loams. Combining these data into a water-balance model has led to a simple expression for predicting drainage at tank farms. Based on the past 20-year record, we predict drainage rates for tank farms ranging from 20 to 80 mm/yr (0.8 to 3.1 in./yr). The model does not account for thermal effects on evaporation due to radiolytically heated tank wastes (i.e., warmer subsurface temperatures could increase the evaporation rates from tank farms, thus decreasing drainage). For this reason, the values reported here may overestimate the true drainage flux.

There have been no measurements of drainage at Hanford tank farms, so verification of the model remains to be completed. The surface-water balance must be modeled in more detail because employing deterministic codes requires hydrologic data such as water-retention characteristics and unsaturated hydraulic conductivities of the surface soil, presently unavailable in any of the tank farms. Examples of deterministic codes include UNSAT-H (Fayer and Gee 1997), HELP (Schroeder et al. 1994), or a transient water-budget model (Simmons and Meyer 2000). Even if hydrologic data were available, it is apparent that calibration is required (Fayer et al. 1992; Fayer and Gee 1997; Simmons and Meyer 2000) for such models to correctly predict drainage at Hanford tank farms.

Several options are available for improving tank-farm drainage predications. First, it is important to continue to maintain the lysimeter records upon which models can be calibrated. Longer records, including additional climatic variations and their impact on drainage, can build confidence in the range over which a drainage model will perform. Second, as a minimum, obtain textural data from surface soils at SX and other tank farms of interest. It also would be helpful, in using more sophisticated methods (as described above), to obtain water-retention and unsaturated-hydraulic-conductivity data for surface soils required for model inputs. Finally, short of installing a large lysimeter facility within a *tank* farm, it would be useful to obtain a direct measure of the water flux within the tank farm. This could be accomplished by installing small water-flux meters (Gee et al. 2000) within several of the tank farms. These devices measure water-flux rates from less than 10 mm/yr (0.4 in./yr) to more than 10,000 mm/yr (394 in./yr), providing short-term (multiple-year) drainage data upon which numerical models can be calibrated. Such an effort will provide improved predictions of the net infiltration that drives contaminants to groundwater at tank farms at Hanford.

D.8.2.4 Conclusions and Implications

Estimates were made of net infiltration (drainage) of meteoric water at the SX tank farm using a simple water-balance model. The model was based on climatic variables and surface soil textures specific to the Hanford Site. Winter (November through March) precipitation records for the past 20 years were combined with soil-texture data obtained from tank farm soil samples. These data were required to calibrate the water-balance model, which was subsequently used to estimate drainage flux at the SX tank farm. SX tank farm soil texture was assumed to be sandy gravel with 3% fines. When the water-balance model was applied to the SX tank farm, the drainage averaged 56 mm/yr (2.2 in./yr) for the past 20 years and ranged from 5 to 162 mm/yr (0.2 to 6.4 in./yr). The drainage estimate is conservative since it does not include the influence of elevated temperatures in the subsurface (due to radiolytic soil heating). Improvements in the estimates of drainage at the SX tank farm are expected when detailed soil-textural analyses of the SX tank farm surface soil are completed and when direct measurements with water-flux meters are implemented.

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D.8.3 EFFECTS OF ACCELERATED MOVEMENT DUE TO SURFACE TENSION AND CONTACT ANGLE EFFECTS IN HYPERSALINE FLUIDS TRANSPORTED IN UNSATURATED SEDIMENTS

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D.8.3.1 Introduction

Highly saline fluids have leaked into the ground at the SX tank farm (Seme et al. 1997; Myers et al. 1998). These highly saline fluids have properties quite different from pure water or water from meteoric inputs (rain or snowmelt). Density (e.g., specific gravity) can be in excess of 1.3, relative viscosity greater than 3, surface tension in excess of 100 dynes/cm, and contact angle greater than zero. Meteoric waters added to the subsurface will eventually dilute the tank leak and reduce the impact of the extreme chemistry. However, the fluid properties of the leaked tank liquor must be known to adequately predict the contaminant migration rates in Hanford sediments. During the first 2 years of this EMSP project, efforts were made to evaluate the impact of the salt plume, both in the laboratory and in the field. While these experiments are ongoing, the observations to date can be used to infer the performance of highly saline fluids within the vadose zone.

D.8.3.2 Discussion of High Salt Tests

Both laboratory and field tests were initiated to assess the impact of hypersaline fluids on migration rates in Hanford sediments. In the field, a series of tests were conducted to evaluate the movement of dense fluids in Hanford sediments. Sodium nitrate solution (5 N concentration with a specific gravity of 1.3) was infiltrated into Hanford sediments in the field in the spring of 1999. The highly saline solution rapidly infiltrated, but due to textural layering, the plume was dispersed laterally in all cases, even when the surface tension was altered by use of organic additives. The impacts of density and surface tension were mitigated by layering, which prevented finger formation and deep penetration of the nitrate solution. In the laboratory, coarse sediments from the Hanford formation were placed in cells that were exposed to X-ray Microfocus Tomography (XMT). These tests demonstrated that fingers could develop with hypersaline solutions when coarse Hanford sediments were packed without layering. However, with layering, the fingering was prevented. A theoretical assessment of fingering was conducted using computer models developed by PNNL. The computer code STOMP (White et al. 1995; White and Oostrom 1996) was modified to describe the movement of hypersaline solutions. The modeled finger formed when hypersaline solution with known density and surface tensions were tested in the model. Known hydrologic parameters for a coarse Hanford sediment were also used as model input. Figure D.8.3.1 shows the plume development when water (left) was introduced into the simulated test column compared to the hypersaline solution (right). The model is capable of predicting the finger development. When layered soils are simulated in the model, the finger does not form, qualitatively predicting the observed layer control on fingering that has been observed both in the laboratory and field. The results suggest that layering has a significant impact on the movement of the hyper-saline leak in the SX tank farm. It is very likely that some deep penetration occurred beneath the tank, but the lithology of the

subsurface sediments reflects a highly layered system. So it is not surprising that no deep penetration or preferential flow of high salt occurred. At least any deep penetration cannot be attributed solely to surface tension or density effects. This work will continue through the end of FY 2001.

Figure D.8.3.1. Simulated Plume Development in Hanford Sediments Using STOMP.

Note: Plot on left is plume developed for low concentration salt system (river water) infiltrating into a 0.6-m (2-ft) deep soil column for a period of 60 minutes. Plume on right is for similar time sequence, but with 5 N NaNO_3 .

D.8.3.3 Conclusions and Implications

Traditional transport models have failed to provide adequate descriptions of contaminant distributions in the vadose zone of Hanford's tank farms. Tank fluids leaked to the vadose zone are hypersaline with normality at or above 10 and specific gravity ranging from 1.3 to 1.5. In this study, it is hypothesized that deviation between observed and predicted plume distributions is related to the fluid constitution, its effect on surface tension, equilibrium contact angle, and ultimately on the water-retention function. A thermodynamic model that describes interfacial tension and equilibrium contact angle as functions of aqueous-phase salt concentrations is incorporated into the STOMP numerical simulator and used to predict the infiltration of hypersaline fluids through the vadose zone. Specific wetting-front features, which are absent in the pure-fluid case, are identified and quantified. Laboratory observations and numerical simulations suggest that the elevated surface tensions observed in hypersaline fluids may play a fundamental role in water and contaminant migration at the SX tank farm and wherever these high-salt fluids have leaked into the ground.

D.8.3.4 Acknowledgements

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D.8.3.5 References

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D.8.4 CONCLUSIONS OF S&T INVESTIGATIONS OF VADOSE ZONE FIELD EXPERIMENTS AND INFILTRATION ESTIMATES FOR THE SX TANK FARM

Hydrologic research efforts that provide additional support to characterization efforts at the SX tank farm include (1) the Vadose Zone Transport Field Study (VZTFS), (2) studies to develop simplified methods for estimating recharge rates at the SX and other tank farms and (3) an EMSP supported study of the hydrologic impacts of highly concentrated salt solutions in Hanford sediments.

VZTFS Studies. VZTFS field studies at the Hanford Site are evaluating the movement of contaminant plumes in the vadose zone in order to better predict the transport of contaminants in tank farms and other waste-disposal sites. The first of four field tests was completed at the 299-E24-111 injection site in the 200 East Area during FY 2000. Five discrete pulses, totaling nearly 19,000 L (5,000 gal), added to injected to the ground during the test. Nine geophysical methods were used in the study, all of which were successful in identifying changes in subsurface water contents. Changes in water content were found to be minimal below 11 m (36 ft), which suggests that lateral flow in shallow soil dominates much of the transport. The two-dimensional numerical model applied to the test site appears to capture the plume's general flow depths and directions, but is deficient in describing the extent of the plume's lateral spreading. It is anticipated that hydraulic property data collected during this testing may help improve future predictions of lateral spreading. The implications of this VZTFS study support the general observations that chemicals such as cesium can move laterally in Hanford sediments, as moves was observed near tank SX-109. The lateral movement of radionuclides is an indication that there is lithologic control of the hydraulic properties, similar to what was observed in our field test.

Simplified Methods for Estimating Recharge. While contaminants such as cesium have been held up in the vadose zone in the SX tank farm, others such as ^{99}Tc , chromate, and nitrate have reached groundwater. It is hypothesized that winter rains and snowmelt runoff, and in some cases water-line leaks, have infiltrated deeply and in specific areas have leached soil contamination from the vadose zone to the underlying water table. Water moves through the soil more rapidly beneath buried tanks because the area is devoid of plants and covered with gravel. The drainage (recharge) rate of meteoric water at the SX tank farm was estimated using a simple water-balance model that was based on the climate and surface soil textures at the Hanford Site. Assessing the complete water balance of the surface soils provides the best way to analyze deep drainage. Three main factors (climate, soils, and vegetation) were evaluated to assess the water balance. Climate studies indicate that most summer precipitation evaporates, leaving winter precipitation as the only significant contributor to water drainage in the soils. The soils around the tank farms are mostly coarse soil and gravel, which allows water to migrate easily under gravity. No vegetation is allowed to grow around the tank farms; therefore, no water is taken up by plants. Winter precipitation records were combined with soil-texture data obtained from tank-farm soil samples. At the SX tank farm, the drainage estimate averaged 56 mm/yr (2.2 in./yr) for the past 20 years and ranged from 5 to 162 mm/yr (0.2 to 6.4 in./yr). This estimate is conservative since it does not include the influence of elevated temperatures in the subsurface because of heating from radioactive wastes in tanks.

Impacts of Highly Concentrated Salt Solutions on Flow Stability in Hanford Sediments. Traditional transport models have not provided adequate descriptions of contaminant distributions in the vadose zone because leaking tank fluids are hypersaline. The properties of these fluids are quite different from meteoric inputs. The effects of these hypersaline solutions needs to be better understood to account for a significant deviation between observed and predicted plume distributions. Preliminary studies suggest that layering has a significant impact on the transport of hyper-saline fluids. Laboratory observations and numerical simulations suggest that the elevated surface tensions observed in hypersaline fluids may play a fundamental role in water and contaminant migration at the Hanford Site.

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APPENDIX E

IMPACT ASSESSMENT APPROACH AND RESULTS

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LIST OF TERMS

BTC	breakthrough curve
CoPCs	contaminants of potential concern
DOE	U.S. Department of Energy
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
HSRAM	Hanford Site Risk Assessment Methodology
ILCR	incremental lifetime cancer risk
MTCA	Model Toxics Control Act
TWRS EIS	Tank Waste Remediation System Environmental Impact Statement
WMA	waste management area

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E.I.O INTRODUCTION

A series of numerical simulations are conducted to evaluate the performance of interim corrective measures such as surface barriers in reducing long-term human health risks from potential groundwater contamination at waste management area (WMA) S-SX. The specific objectives of the numerical assessment are to: (1) quantify the risks posed by past tank releases to the groundwater if no interim corrective measures are implemented, and (2) determine to what degree implementation of selected interim corrective measures would decrease the risks posed by past tank releases. The assessments focus specifically on impacts to groundwater resources (i.e., the concentration of contaminants in groundwater) and long-term risk to human health (associated with groundwater use). The evaluations consider the extent of contamination presently within the vadose zone, contaminant movement through the vadose zone to the saturated zone (groundwater), contaminant movement in the groundwater to points of compliance, and the types of assumed human receptor activities at the points of compliance. The impact assessment results present several key evaluations for decision-maker input that may impact current operations and future decisions on tank retrieval and closure.

E.2.0 MODELING APPROACH

Both base case (existing tank farm conditions) and engineered alternatives for the interim corrective measures are considered. The focus for the contaminant transport modeling is chemicals (i.e., nitrate and chromium) and long-lived radionuclides (i.e., technetium-99) that are environmentally mobile. The postulated conceptual model utilizes the recently collected data on technetium-99 and other constituents from borehole 41-09-39, borehole 299-W23-19 near tank SX-115, and the MACTEC-ERS cesium-137 plume maps (Goodman 2000).

For simulations with barriers, it is assumed that an interim barrier is in place by the year 2010. It is also assumed that for all simulations, as part of tank farm closure, a closure barrier is in place by the year 2040. Placing a barrier is expected to significantly reduce infiltration of meteoric water and therefore arrival of contaminants at the water table. The modeling considers the estimated inventories of contaminants within the vadose zone and calculates the associated risk (i.e., exceeding the drinking water standards [40 CFR 141] at the compliance point). Inventory estimates are considered to be a critical factor in calculations, and uncertainties in inventories are considered. It is assumed that no tank leaks will occur in the future. It is also assumed that, as part of 'good housekeeping,' water-line leaks from existing piping will be addressed and resolved. However, as discussed later, as part of sensitivity analysis, simulations are run to evaluate long-term effects of water-line leaks in the vicinity of tank SX-115. The umbrella structure of the tank and shedding of water are simulated. Sediments adjacent to the tanks attain elevated water contents and, while remaining unsaturated, they develop what is known as moisture-dependent anisotropy. Such effects are simulated in the model. Numerical results are obtained for compliance at the WMA boundary, 200 West fence boundary, exclusion boundary beyond the 200 Areas, and the Columbia River. Except for the 200 West fence boundary, these boundaries are based on DOE-RL (2000). Instead of the 200 West fence boundary, DOE-RL (2000) refers to the 200 Areas boundary. However, since the 200 Areas and the exclusion boundaries are relatively close the 200 Areas boundary is replaced by the 200 West fence boundary. Streamtube/analytical models are used to route computed contaminant concentrations at the water table to compliance points.

Two-dimensional cross-sectional models are used to model vadose zone flow and transport. Three representative (west-east) cross-sectional models for the S and SX tank farms (Figure E.1) are considered:

- Cross-section through tanks SX-107, SX-108, and SX-109
- Cross-section through tanks SX-113, SX-114, and S-115
- Cross-section through tanks S-104, S-105, and S-106.

Note that, in this appendix and elsewhere in the main text (Section 4.0), the three cross-sections are labeled in two ways. For example, the row containing tanks SX-107, SX-108, and SX-109 is often labeled as cross-section SX-DD'. Similarly, cross-section SX-FF' refers to the row containing tanks SX-113, SX-114, and SX-115 and cross-section S-CC' refers to the row containing tanks S-104, S-105, and S-106. Figures E.2 through E.4 show the three geologic cross-sections.

Figure E.1. Location Map of Single-Shell Tank WMA S-SX and Surrounding Facilities in the 200 West Area

Figure E.2. Cross-Section SX-DD'

Figure E.3. Cross-Section SX-FF'

Figure E.4. Cross-Section S-CC'

Simulation of flow and transport through each cross-section generates a breakthrough curve (BTC) at the water table. The temporal and spatial distribution for each of these BTCs is recognized and the principle of superposition is used to generate a composite BTC at the compliance boundary. An analytical/streamline approach is used to route the BTCs through the unconfined aquifer to the compliance boundary. The BTCs are converted into dose estimates using appropriate factors.

Fluid flow within the vadose zone is described by Richards' equation, whereas the contaminant transport is described by the conventional advective-dispersive transport equation with an equilibrium linear sorption coefficient (K_d) formulation. Detailed stratigraphic cross-sectional model data are based on information in *Subsurface Physical Conditions Description of the S-SX Waste Management Area* (Johnson et al. 1999), *Geology of the 241-S Tank Farm* (Price and Fecht 1976a), and *Geology of the 241-SX Tank Farm* (Price and Fecht 1976b). The model includes the effects of dipping strata. The enhanced spreading at the fine-grained/coarse-grained interfaces and the increased downdip movement of the plume along these interfaces are included in the model.

Data on laboratory measurements for moisture retention, particle-size distribution, saturated and unsaturated hydraulic conductivity, and bulk density for individual stratum are based on data on 200 East and 200 West Area soils (Khaleel et al. 2000). For each stratum defined by the stratigraphic cross-sectional model, the small-scale laboratory measurements are upscaled to obtain equivalent horizontal and vertical unsaturated hydraulic conductivities as a function of mean tension (Khaleel et al. 2000). Upscaling of unsaturated hydraulic conductivities (K 's) leads to development of macroscopic anisotropies (as a function of mean tension) for each layer. An averaging of van Genuchten parameters (θ_r , θ_s , α , and n) (van Genuchten 1980) is used to define a moisture retention curve for each stratum.

In case multiple samples are not available for each stratum, data from other sites in the WMA S-SX vicinity are used. Attempts are made to use hydraulic properties that were obtained using both laboratory-measured moisture retention and unsaturated hydraulic conductivity. This is primarily to avoid extrapolating the unsaturated conductivities (van Genuchten 1980; Mualem 1976) to the dry end, based on saturated conductivity estimate (Khaleel et al. 1995). Also, to reflect field conditions, the laboratory data are corrected for the presence of any gravel fraction in the sediment samples (Khaleel and Relyea 1997).

As with flow modeling, each stratum is modeled with different transport parameters (i.e., bulk density, diffusivity, and dispersivity). As discussed earlier, contaminant mobility is quantified by sorption coefficients. A highly disturbed geochemical environment exists in the WMA S-SX vadose zone. The zones exist because chemistry of some leaked fluids radically differs from water and could change the soil water geochemical regime as migration occurs. The available database suggests that the most severe changes have occurred in soils underlying and near tanks SX-107, SX-108, and SX-109. While there is uncertainty about the sorption coefficient of cesium-137 and how it changes with concentration of competing ions, there is no doubt the sorption coefficient of technetium-99 is close to 0 mL/g in Hanford Site sediments. The low sorption coefficient coupled with a long half-life (2.03×10^5 years) allows technetium-99 to migrate over long distances in both the vadose zone and groundwater, posing a threat to groundwater quality for a long time.

Initial Conditions

Initial conditions are needed for moisture content (or pressure head) and contaminant concentration. For simulations not considering a barrier, initial conditions for pressure head (and moisture content) are established by allowing the vadose zone to equilibrate with an infiltration rate representative of natural infiltration for tank farm conditions. The data on infiltration rates with and without barriers are included in Section E.2.2.1. Initial conditions for contaminant concentration are provided as part of inventory estimates for cesium-137, technetium-99, nitrate, and chromium.

Model Setup and Boundary Conditions

A two-dimensional (west-east) vertical (x-z) slice of the flow domain is used for modeling flow and transport. The simulation domain extends horizontally to include the WMA S-SX boundaries and the water table, which is located about 65 m (213 ft) below ground surface. The geologic strata are assumed continuous but not of constant thickness. A variable grid spacing is used to model features such as the presence of clastic dikes between tanks. Sloped interfaces for geologic units are included based on information in Johnson et al. (1999), Price and Fecht (1976a), and Price and Fecht (1976b).

For flow modeling, Neumann boundary conditions are prescribed at the surface with the flux equal to the recharge rate estimate. For transport modeling, a zero flux boundary is prescribed at the surface for cesium-137, technetium-99, nitrate, and chromium. The western and eastern boundaries are assigned no-flux boundaries for both flow and transport. The water table boundary is prescribed by water table elevations and the unconfined aquifer hydraulic gradient. No-flux boundaries are used for the lower boundary.

To account for the residual effects of tank leaks, the variable density and viscosity of the leaked fluid are considered. The increased fluid density effects are expected to enhance the vertical mobility of both the fluid and the contaminant. The density effect can elongate the plume vertically and tends to decrease the lateral spreading caused by stratigraphic variations in material properties and moisture-dependent anisotropy.

Clastic dikes are included in the modeling as a sensitivity analysis. Clastic dikes occur in many locations in the 200 West Area and have been hypothesized as potential pathways for vertical transport that could explain the deep migration of contaminants at the SX tank farm. Preliminary data on clastic dike infilling materials are based on *Far-Field Hydrology Data Package for Immobilized Low-Activity Tank Waste Performance Assessment* (Khaleel 1999). Detailed inputs for various flow and transport parameters are presented later.

E.2.1 NUMERICAL CASES CONSIDERED

The following simulation runs (Cases 1 through 13) are considered for two-dimensional simulations. Note that Cases 1 through 4 consider a spatially uniform distribution of the inventory for the three cross-sections. Cases 5, 6, and 7 consider a nonuniform distribution of the same inventory. Case 7 considers a different location of the inventory within the two-dimensional cross-section. Cases 3 and 13 consider different volumes for water-line leaks, whereas Cases 9 through 11 consider varying estimates of natural recharge. Note that for Cases 3 and 13, the three-dimensional water-line leak was modeled as a point source of water spread over a circular area between two tanks. The circular leak area was translated for the two-dimensional simulations using a unit computational grid width and assuming that the center of the leak area was situated on the center line between tanks. Details are given in Section E.4.0. The simulations are run for a period of compliance of 1,000 years. Note that each of the 13 cases summarized below involves three cross-sectional runs.

- **Case 1:** Base Case, **No** Action Alternative. Flow and transport runs for cross-sections through tanks SX-107, SX-108, and SX-109; tanks SX-113, SX-114, and SX-115; and tanks S-104, S-105, and S-106 considering natural infiltration *only*, *no* water-line leak, *no* interim barrier, and a closure barrier by the year 2040.
- **Case 2:** Barrier Alternative and No Water-Line Leak. Flow and transport runs for cross-sections through tanks SX-107, SX-108, and SX-109; tanks SX-113, SX-114, and SX-115; and tanks S-104, S-105, and S-106 considering placement of an interim barrier by 2010; a closure barrier by 2040 (i.e., the interim barrier replaced by the closure barrier); and *no* water-line leak.
- **Case 3:** No Barrier and **25,000** gal Water-Line Leak. Flow and transport runs for cross-sections through tanks SX-107, SX-108, and SX-109; tanks SX-113, SX-114, and SX-115; and tanks S-104, S-105, and S-106 considering natural infiltration, water-line leak (25,000 gal) for tank SX-115 *only*, and *no* barrier until closure.
- **Case 4:** **No** Interim Barrier and Clastic Dikes. Flow and transport runs for cross-sections through tanks SX-107, SX-108, and SX-109; tanks SX-113, SX-114, and

SX-115; and tanks S-104, S-105, and S-106 considering natural infiltration, clastic dikes midway between tanks SX-108 and SX-109, and *no* interim barrier until closure.

- **Case 5: Nonuniform Inventory Distribution and No Barrier.** Flow and transport runs for cross-sections through tanks SX-107, SX-108, and SX-109; tanks SX-113, SX-114, and SX-115; and tanks S-104, S-105, and S-106 considering natural infiltration *only*; *no* water-line leak; *no* barrier until closure; and a higher distribution of inventory at a few locations (e.g., a few nodes, with a high concentration, either at the same depth or at different depths).
- **Case 6: Nonuniform Inventory Distribution and Barrier.** Flow and transport runs for cross-sections through tanks SX-107, SX-108, and SX-109; tanks SX-113, SX-114, and SX-115; and tanks S-104, S-105, and S-106 considering barrier infiltration (interim barrier replaced at closure); *no* water-line leak, and a higher distribution of inventory at a few locations (e.g., a few nodes, with a high concentration, either at the same depth or at different depths).
- **Case 7: Displaced-Nonuniform Inventory Distribution and No Barrier.** Flow and transport runs for cross-sections through tanks SX-107, SX-108, and SX-109; tanks SX-113, SX-114, and SX-115; and tanks S-104, S-105, and S-106 considering natural infiltration *only*, *no* water-line leak, *no* barrier until closure, and an inventory location close to the water table.
- **Case 8: Density and Viscosity Effects.** Flow and transport runs for cross-sections through tanks SX-107, SX-108, and SX-109; tanks SX-113, SX-114, and SX-115; and tanks S-104, S-105, and S-106 considering natural infiltration *only*, *no* water-line leak, enhanced density and viscosity, and *no* barrier until closure.
- **Case 9: Base Case with 50 mm/yr Meteoric Recharge.** Flow and transport runs for cross-sections through tanks SX-107, SX-108, and SX-109; tanks SX-113, SX-114, and SX-115; and tanks S-104, S-105, and S-106 considering natural infiltration (50 d y r) *only*, *no* water-line leak, *no* interim barrier, and a closure barrier by the year 2040.
- **Case 10: Base Case with 30 mm/yr Meteoric Recharge.** Flow and transport runs for cross-sections through tanks SX-107, SX-108, and SX-109; tanks SX-113, SX-114, and SX-115; and tanks S-104, S-105, S-106 considering natural infiltration (30 mm/yr) *only*, *no* water-line leak, *no* interim barrier, and a closure barrier by the year 2040.
- **Case 11: Base Case with 10 mm/yr Meteoric Recharge.** Flow and transport runs for cross-sections through tanks SX-107, SX-108, and SX-109; tanks SX-113, SX-114, and SX-115; and tanks S-104, S-105, S-106 considering natural infiltration (10 mm/yr) *only*, *no* water-line leak, *no* interim barrier, and a closure barrier by the year 2040.
- **Case 12: Alternate Inventory Distribution and No Barrier.** Flow and transport runs for cross-sections through tanks SX-107, SX-108, and SX-109; tanks SX-113, SX-114, and SX-115; and tanks S-104, S-105, and S-106 considering natural infiltration (100 d y r) *only*, *no* water-line leak, *no* interim barrier, a closure barrier by the year 2040, and an alternate inventory distribution.

- **Case 13: No Barrier and 200,000 gal Water-Line Leak.** Flow and transport runs for cross-sections through tanks SX-107, SX-108, and SX-109; tanks SX-113, SX-114, and SX-115; and tanks S-104, S-105, and S-106 considering natural infiltration (100 mm/yr), water-line leak (200,000 gal) for tank SX-115 *only*, and *no* barrier until closure.

In addition to the preceding two-dimensional simulations, a fully three-dimensional simulation (see Section E.4.14) is also considered. However, the risk calculations are all based on two-dimensional simulation results. The three-dimensional simulation is performed as a check on the two-dimensional analysis.

E.2.2 RECHARGE ESTIMATES AND VADOSE ZONE FLOW AND TRANSPORT PARAMETERS

Modeling inputs for recharge estimates and effective (upscaled) flow and transport parameters are presented in this section. The effective parameters are based on laboratory measurements of moisture retention, saturated and unsaturated hydraulic conductivity, and bulk density for sediment samples in the 200 Areas.

E.2.2.1 Recharge Estimates

The S and SX tank farm surfaces are covered with gravel to prevent vegetation growth and provide radiation shielding for site workers. Bare gravel surfaces, however, enhance net infiltration of meteoric water compared to undisturbed naturally-vegetated surfaces. Infiltration is further enhanced in the tank farms by the effect of percolating water being diverted by an impermeable, sloping surface of the tank domes. The basis for recharge estimates (Table E.1) for field investigation report modeling is presented in the main text (Section 3.1.2).

Condition Simulated	Recharge Estimate (mm/yr)
No barrier 12000-20101	100
Interim barrier 12010-20401	0.5
Closure barrier (1 st 500 yrs) [2040-2540]	0.1

E.2.2.2 Vadose Zone Flow and Transport Parameters

This section provides effective (upscaled) values of flow and transport parameters for the vadose zone. Specific flow parameters include moisture retention and saturated and unsaturated hydraulic conductivity. Transport parameters include bulk density, diffusivity, sorption coefficients, and macrodispersivity. Details on deriving the effective (upscaled) parameters are addressed in *Modeling Data Package for S-SX Field Investigation Report (FIR)* (Khaleel et al. 2000).

Table E.2 lists composite, fitted van Genuchten-Mualem (van Genuchten 1980; van Genuchten et al. 1991) parameters for various strata at the S and SX tank farms. Again, note that the material type numbers noted in Table E.2 (and in Tables E.3, E.5, and E.6) are identical to those indicated in the modeling data package (Appendix B of Khaleel et al. 2000). Estimates for the equivalent horizontal and vertical hydraulic conductivities are presented in Section E.2.2.3.

Table E.2. Composite van Genuchten-Mualem Parameters for Various Strata at the S and SX Tank Farms

Strata/Material Type	Number of Samples	θ_s	θ_r	α (1/cm)	n	ℓ	Fitted K_s (cm/s)
Backfill (1)	10	0.1380	0.0100	0.0210	1.3740	0.5	5.60E-04
Sand (2)	12	0.3819	0.0443	0.0117	1.6162	0.5	9.88E-05
Gravelly sand/sandy gravel (3)	11	0.2126	0.0032	0.0141	1.3730	0.5	2.62E-04
Plio-Pleistocene (4)	4	0.4349	0.0665	0.0085	1.8512	0.5	2.40E-04
Sandy gravel (5)	10	0.1380	0.0100	0.0210	1.3740	0.5	5.60E-04

Source: Khaleel et al. (2000).

E.2.2.3 Stochastic Model for Macroscopic Anisotropy

Variable, tension-dependent anisotropy provides a framework for upscaling small-scale, laboratory measurements to the effective (upscaled) properties for the large-scale tank farm vadose zone. A stochastic model (Polmann 1990) is used to evaluate tension-dependent anisotropy for sediments at the WMA S-SX; details are in Appendix C of Khaleel et al. (2000). The following is a brief description of the variable anisotropy model used in the field investigation report modeling.

Yeh et al. (1985) analyze steady unsaturated flow through heterogeneous porous media using a stochastic model; parameters such as hydraulic conductivity are treated as random variables rather than as deterministic quantities. The Gardner (1958) relationship is used in Yeh et al. (1985) to describe unsaturated hydraulic conductivity (K) as a function of saturated hydraulic conductivity (K_s) and tension (ψ), that is,

$$K(\psi) = K_s \exp(-\beta\psi) \quad (\text{E.1})$$

where:

β = fitting parameter.

Equation E.1 can be written as

$$\ln K(\psi) = \ln K_s - \beta\psi \quad (\text{E.2})$$

Equation E.2 is referred to as the log-linear model, because $\ln K$ is linearly related to ψ through the constant slope β . However, such a constant slope is often inadequate in describing $\ln K(\psi)$ over ranges of tension of practical interest for field applications. As an alternative, the slope β can be approximated locally by straight lines over a fixed range of tension. The $\ln K_s$ in Equation E.2 can then be derived by extrapolating the local slopes back to zero tension.

Using a linear correlation model between the log-conductivity zero-tension intercept and β , Polmann (1990) presents a generalized model that accounts for the cross-correlation of the local soil property (i.e., $\ln K_s$ and β) residual fluctuations. Compared to uncorrelated $\ln K_s$ and β model, partial correlation of the properties is shown to have a significant impact on the magnitude of the effective parameters derived from the stochastic theory. The Polmann (1990) equations for deriving the effective parameters are as follows.

$$\begin{aligned} \langle \ln K \rangle &= \langle \ln K_s \rangle - A \langle \psi \rangle - \sigma_{\ln K_s}^2 \lambda [p - p^2 \langle \psi \rangle - \zeta^2 \langle \psi \rangle] / (1 + A\lambda) \\ \sigma_{\ln K}^2 &= \sigma_{\ln K_s}^2 [(1 - p \langle \psi \rangle)^2 + \zeta^2 \langle \psi \rangle^2] / (1 + A\lambda) \\ K_h^{eq} &= \exp[\langle \ln K \rangle + (\sigma_{\ln K}^2 / 2)] \\ K_v^{eq} &= \exp[\langle \ln K \rangle - (\sigma_{\ln K}^2 / 2)] \end{aligned} \quad (E.3)$$

where:

- $\sigma_{\ln K}^2$ = variance of log unsaturated conductivity (which depends on mean tension)
- $\langle \psi \rangle$ = mean tension
- $\sigma_{\ln K_s}^2$ = variance of $\ln K_s$
- $\langle \ln K_s \rangle$ = mean of $\ln K_s$
- p = slope of the β versus $\ln K_s$ regression line
- ζ = $\sigma_\delta / \sigma_{\ln K_s}$
- σ_δ = standard deviation of the residuals in the β versus $\ln K_s$ regression
- A = mean slope, β , for $\ln K_s$ vs. ψ
- λ = vertical correlation lengths for $\ln K_s$ (assumed to be same as that of β)
- K_h^{eq} = equivalent unsaturated horizontal conductivity
- K_v^{eq} = equivalent unsaturated vertical conductivity.

E.2.2.3.1 Macroscopic Anisotropy Parameters. Table E.3 lists the variable, macroscopic anisotropy parameter estimates for various strata at WMA S-SX. Details on derivation of the parameter estimates are included elsewhere (Appendix C of Khaleel et al. 2000).

**Table E.3. Macroscopic Anisotropy Parameters Based on Polmann (1990)
Equations for Various Strata at the S and SX Tank Farms**

Strata/Material Type	Number of Samples	$\langle \ln K_s \rangle$	$\sigma^2_{\ln K_s}$	p	ζ	λ (cm)	A
Backfill (1)	10	-15.76	3.56	-1.1E-4	1.84E-4	30	0.00371
Sand (2)	12	-14.6	1.50	-7.2E-4	6.55E-4	50	0.00620
Gravelly sand/sandy gravel (3)	11	-14.85	1.94	-2.6E-4	2.50E-4	30	0.00368
Plio-Pleistocene (4)	4	-10.43	1.01	2.4E-3	9.34E-4	50	0.0104
Sandy gravel (5)	10	-15.76	3.56	-1.1E-4	1.84E-4	30	0.00371

E.2.2.4 Clastic Dike Infilling Material Properties

Data on physical and hydraulic parameters are needed for clastic dike infilling materials to model their effects on flow and contaminant transport. Data on bulk density, particle-size distribution, moisture retention, saturated and unsaturated hydraulic conductivities for clastic dike infilling materials are included in Appendix C of Khaleel et al. (2000). Table E.4 provides the effective parameters.

Table E.4. Effective Hydraulic Parameters for Clastic Dike Infilling Materials

Material	θ_s (cm ³ /cm ³)	θ_r (cm ³ /cm ³)	a (1/cm)	n (-)	Saturated Hydraulic Conductivity (cm/s)
Clastic dike	0.4348	0.04675	0.07343	1.7115	1.20E-03

E.2.2.5 Enhanced Density and Viscosity Estimates

Numerical simulation cases in Section E.2.1 identify one run with enhanced density and viscosity estimates for the leaked fluid. The impact of fluid properties (density and viscosity) on contaminant migration is investigated by considering a fluid specific gravity of 1.4 (Ward et al. 1997).

E.2.2.6 Effective Transport Parameters

Effective transport parameter (bulk density, diffusivity, and dispersivity) estimates are presented in this section. Because of natural variability, the transport parameters are all spatially variable. The purpose is again, similar to the flow parameters, to evaluate the effect of such variability on the large-scale transport process.

E.2.2.6.1 Bulk Density and Sorption Coefficient. Both bulk density (ρ_b) and sorption coefficient estimates are needed to calculate retardation factors for different species. The effective, large-scale estimate for the product $[\rho_b K_d]$ is the average of the product of

small-scale laboratory measurements for bulk density and sorption coefficient (Gelhar 1993). Table E.5 provides the effective, large-scale estimates for cesium-137. The average ρ_b , $E[\rho_b]$ (Table E.5) estimates are based on data in Khaleel et al. (2000) for the five strata and clastic dike samples. The sorption coefficient estimates (Table E.5) for cesium-137 are based on *Data from Geochemical Data Package for the Immobilized Low-Activity Waste Performance Assessment* (Kaplan and Serne 1999) for undisturbed sediments. No other species are included, because the sorption coefficients for technetium-99, chromium, and nitrate are estimated to be zero. Calculations (Table E.5) for $E[\rho_b]$ and $E[\rho_b K_d]$ include correction for the gravel fraction.

Table E.5. Effective Parameter Estimates, $E[\rho_b K_d]$, for Cesium-137 for the Product of Bulk Density (g/cm^3) and K_d (cm^3/g) at WMA S-SX

Strata/Material Type	K_d	$E[\rho_b]$	$E[\rho_b K_d]$
Backfill (1)	500	1.94	971
Sand (2)	500	1.76	864
Gravelly sandsandy gravel (3)	500	2.07	600
Plio-Pleistocene (4)	500	1.65	814
Sandy gravel (5)	500	2.13	488
Clastic dike	500	1.52	759

E.2.2.6.2 Diffusivity. It is assumed that the effective, large-scale diffusion coefficients for all strata at the S and SX tank farms are a function of volumetric moisture content, θ , and can be expressed using the empirical relation from “Permeability of Porous Solids” (Millington and Quirk 1961):

$$D_e(\theta) = D_0 \frac{\theta^{10/3}}{\theta_s^2} \quad (\text{E.4})$$

where:

$D_e(\theta)$ = effective diffusion coefficient of an ionic species

D_0 = effective diffusion coefficient for the same species in free water.

The molecular diffusion coefficient for all species in pore water is assumed to be $2.5 \times 10^{-5} \text{ cm}^2/\text{sec}$ (Kincaid et al. 1995).

E.2.2.6.3 Macrodispersivity. An extended review is provided in Appendix C of Khaleel et al. (2000) on the rationale for vadose zone macrodispersivity estimates. Macrodispersivity estimates are needed for both reactive (cesium-137) and non-reactive (i.e., technetium-99, chromium, and nitrate) species.

E.2.2.6.3.1 Macrodispersivity Estimates for Non-Reactive Species. Macrodispersivity estimates for non-reactive species (i.e., technetium-99, chromium, and nitrate) are listed in Table E.6. Details on the basis for the estimates are provided in Appendix C of

Khaleel et al. (2000). Macrodispersivities for clastic dike sediments are assumed to be same as those for the Plio-Pleistocene unit.

Table E.6. Non-Reactive Macrodispersivity Estimates for Various Strata at the S and SX Tank Farms

Strata/Material Type	A_L (cm)	A_T (cm)
Backfill (1)	-150	15
Sand (2)	-150	15
Gravelly sand (3)	-100	10
Plio-Pleistocene (4)	-50	5
Sandy gravel (5)	-150	15

E.2.2.6.3.2 Heterogeneous Sorption Enhanced Macrodispersivities for the Reactive Species. As expected, the net effect of sorption is to retard the velocity of the contaminant. Because sorption for specific contaminants may be a function of soil properties, as the soil properties experience spatial variability, the sorption also varies (Gelhar 1993; Talbott and Gelhar 1994).

Stochastic analysis results for macrodispersivity enhancement for the five strata are presented in Table C-7 of Khaleel et al. (2000) for the reactive species (i.e., cesium-137). Note that the unsaturated conductivities were evaluated at -100 cm via the fitted van Genuchten-Mualem relation. The macrodispersivity enhancement ranged from about 1.07 for backfill sediments to about 2.35 for Plio-Pleistocene unit sediments. No dispersivity enhancement is assumed for the clastic dike sediments.

E.2.3 GROUNDWATER FLOW AND TRANSPORT

The preceding section provides vadose zone flow and transport parameters. This section includes flow and transport parameters for the unconfined aquifer. Also included are the unit dose conversion factors.

E.2.3.1 Flow and Transport Parameters

Instead of the Hanford Site-wide groundwater model, an analytical/streamtube approach is used to model groundwater flow and transport. However, as indicated in the following sections, flow and transport information needed for the analytical/streamtube model is based on the VAM3D Site-wide groundwater model (Law et al. 1996).

Figure E.5 shows the VAM3D-generated water table map at steady state, following simulation for 1,000 years. Figure E.5 can be used to generate streamlines/pathlines. Figure E.6 shows a streamline/pathline originating from the S and SX tank farms.

Figure E5. VAM3D-Generated Steady State Hydraulic Head Distribution for the Hanford Site, Following Simulation for 1,000 Years

Source: Lu 1996.

Figure E.6. VAM3D-Generated Pathline Distribution at Steady State, Following Simulation for 1,000 Years

Source: Lu 1996.

Information on groundwater velocity distribution is needed for the analytical/streamtube model. Figure E.7 prescribes the material property numbers for various regions within the flow domain of the Site-wide model. Darcy's law, combined with Figure E.5 and Table E.7, which provides the saturated hydraulic conductivity and porosity for each material type, are used to perform necessary velocity calculations. Other parameters needed for groundwater transport modeling are listed in Table E.8. Note that a small vertical macrodispersivity of 10 mm is used based on the limited vertical mixing observed in stratified aquifers such as those in the 200 Areas (van der Kamp et al. 1994); the other macrodispersivities are the same as those used in the Site-wide model (Law et al. 1996).

E.2.3.2 Unit Dose Factors

Table E.9 lists the unit dose factors needed to convert cesium-137 and technetium-99 concentrations in groundwater to a radiation dose. Table E.9 is based on a drinking water consumption scenario of 730 L/yr.

E.2.4 CONTAMINANT INVENTORY

This section provides details on the basis for vadose zone contaminant inventory estimates and their distributions. Also included are details on how various inventory distributions are implemented in the numerical model.

E.2.4.1 Basis for Inventory Estimates

Vadose zone inventory estimates for the four species (i.e., cesium-137, technetium-99, chromium, and nitrate) are primarily based on *Estimation of SX-Farm Vadose Zone Cs-137 Inventories from Geostatistical Analysis of Drywell and Soil Core Data* (Goodman 2000) and the recently collected borehole data. The Goodman (2000) estimates are used to assign inventory estimates for cesium-137 and the borehole data are used to assign estimates for the mobile species (i.e., technetium-99, chromium, and nitrate).

Goodman (2000) presents kriging analysis of cesium-137 inventory estimates in the vadose zone under the SX farm tanks based on measurements in the drywells, laterals, and borehole 41-09-39 soil cores. The details on inventory used in modeling are presented in *Inventory Estimates for Single-Shell Tank Leah in Sand SX Tank Farms* (Jones 2000) and Khaleel et al. (2000), and are included in Attachment E1. For technetium-99, chromium, and nitrate, the inventory estimates are scaled with respect to measured concentrations in boreholes. Note that data in Attachment E1 are decayed as of January 1, 2000. The decay coefficient for cesium-137 is 0.0231 yr^{-1} (i.e., half-life is 30 years).

Results of laboratory analyses of samples from borehole 41-09-39 provide the basis for inventory estimates for the mobile species under tanks SX-107, SX-108, and SX-109. Concentration measurements for samples from borehole 299-W23-19 southwest of tank SX-115 serve as the basis for estimates for the mobile species under tanks SX-113, SX-115, and S-104. Tank S-104 inventory estimates for cesium-137 are based on data from *Tank Summary Data Report for Tank S-104* (DOE-GJPO 1997). Tank SX-115 inventory estimates for cesium-137 are based on data from *Characterization of Subsurface Contamination in the SX Farm* (Raymond and Shdo 1966).

Figure E.7. Material Property Distribution for the Upper Three Elemental Layers for VAM3D Sitewide Groundwater Model

Source: Law et al. 1996.

Zone	K_{xx} (m/y)	K_{yy} (m/y)	K_{zz} (m/y)	S_s (1/m)	Porosity (Percent)
1	.800E+03	.800E+03	.800E+02	.100E-05	10
2	.190E+04	.190E+04	.190E+03	.100E-05	25
3	.500E+04	.500E+04	.500E+03	.100E-05	10
4	.650E+04	.650E+04	.650E+03	.100E-05	10
5	.140E+05	.140E+05	.140E+04	.100E-05	25
6	.720E+05	.720E+05	.720E+04	.100E-05	25
7	.260E+05	.260E+05	.260E+04	.100E-05	10
8	.300E+05	.300E+05	.300E+04	.100E-05	25
9	.430E+05	.430E+05	.430E+04	.100E-05	25
10	.055E+06	.055E+06	.055E+05	.100E-05	25
11	.770E+05	.770E+05	.770E+04	.100E-05	25
12	.899E+05	.899E+05	.899E+04	.100E-05	25
13	.140E+06	.140E+06	.140E+05	.100E-05	25
14	.300E+06	.300E+06	.300E+05	.100E-05	25
15	.750E+06	.750E+06	.750E+05	.100E-05	25
16	.113E+07	.113E+07	.113E+06	.100E-05	25
17	.183E+07	.183E+07	.183E+06	.100E-05	25
18	.213E+07	.213E+07	.213E+06	.100E-05	2s

Parameter	Estimate
Longitudinal macrodispersivity, cm	3050
Lateral macrodispersivity, cm	305
Vertical macrodispersivity	10
Diffusion coefficient, cm ² /sec	2.5×10^{-5}
Cs-137 sorption coefficient, cm ³ /g	500

Radionuclide	Dose factor*
Cs-137	0.0365
Tc-99	0.00107

*Units are mrem per pCi/L of concentration in the groundwater
Source: Rittmann (1999).

E.2.4.2 Inventory Distributions

Because of significant uncertainties with inventory estimates, several distributions were considered. These included (1) uniform, (2) nonuniform, (3) displaced-nonuniform, and (4) an alternate distribution.

E.2.4.2.1 Uniform Distribution. For uniform distribution, the total inventory is assigned to discrete vadose zones, each having different values based on inventory variability. For uniform inventory distribution, the assigned inventory is uniformly distributed within each zone. For the cross-section with tanks SX-107, SX-108, and SX-109 (Figure E.1) the uniform distribution combines, by depth of each zone, the inventory noted in Attachment E1 under both tanks SX-108 and SX-109. The total inventory under both tanks is then distributed in the lateral direction across the two tanks (including the space between the tanks) by depths noted in Attachment E1. Note that both concentration and mass are honored in distributing the inventory in the lateral direction for each depth. For tank SX-107, the inventory is distributed across the diameter of that tank only.

For the cross-section with tanks SX-113, SX-114, and SX-115 (Figure E.1), the individual inventory for tanks SX-113 and SX-115 is distributed in the lateral direction across the tank diameter by depths noted in Attachment E1.

For the cross-section with tank S-104 (Figure E.1), the inventory is distributed uniformly in the lateral direction across the tank diameter by depths noted in Attachment E1.

E.2.4.2.2 Nonuniform Distribution. For nonuniform distribution, the distribution of inventory, by depth, is maintained. However, the inventory within each zone in the lateral direction is nonuniformly distributed but maintains the same mass of inventory as in the uniform distribution. The nonuniform inventory distribution cases are run *only* for the three mobile species.

For the cross-section with tanks SX-107, SX-108, and SX-109, two nonuniform distributions are generated; one for tanks SX-109 and SX-108 and the other for tank SX-107. For tanks SX-109 and SX-108, the nonuniform distribution combines, by depth, the inventory noted in Attachment E1 for tanks SX-109 and SX-108. The total inventory for both tanks is distributed in the lateral direction within the space between tanks SX-109 and SX-108 by depths noted in Attachment E1. For tank SX-107, the total inventory for each depth is distributed in the lateral direction within one-half the space *only* between tanks SX-107 and SX-108, beginning on the western edge of tank SX-107.

For the cross-section with tanks SX-113, SX-114, and SX-115, two nonuniform distributions are generated; one for tank SX-113 and the other for tank SX-115. For tank SX-113, the inventory for each depth is distributed in the lateral direction within one-half the space *only* between tanks SX-113 and SX-114, beginning on the western edge of tank SX-113. Similarly, for tank SX-115 the inventory for each depth is distributed in the lateral direction within one-half the space *only* between tanks SX-114 and SX-115, beginning on the eastern edge of tank SX-115.

For the cross-section with tank S-104, the inventory is distributed in the lateral direction within one-half the space **only** between tanks S-104 and S-105, beginning on the western edge of tank S-104.

E.2.4.2.3 Displaced-Nonuniform Distribution. To examine sensitivity (for mobile species only) relative to depth, a run considers location of the inventory close to the water table. A depth translation of the inventory data in Attachment E1 is used for the **nonuniform** distribution of the inventory for the three mobile species. The peak inventories, as noted in Attachment E1, are positioned within the Ringold Formation at about 50.3 m (165 ft) below ground surface; all other inventory locations are relative to this peak location.

E.2.4.2.4 Alternate Distribution. To further evaluate uncertainty in the lateral extent of the inventory, an alternate distribution was considered. The alternate distribution uses the tank diameters to define the radial extent of the contaminants.

E.2.4.3 Inventory Assignment

This section presents details on how the Attachment E1 inventory estimates were implemented numerically in STOMP (White and Oostrom 2000a, 2000b) calculations. As discussed in Section E.2.4.2, four different inventory distributions were investigated uniform, nonuniform, displaced-nonuniform, and an alternate. Inventory distributions were one of two types: variable diameter or fixed diameter. Variable-diameter distributions honored both the concentration and total solute mass reported for a depth. In contrast, fixed-diameter distributions only honored the total solute mass reported for a depth. The uniform distribution was of the variable-diameter type, whereas the nonuniform, displaced-nonuniform, and alternate were fixed-diameter type distributions.

The uniform distribution most closely represented the inventory distributions (Attachment E1) and comprised of a series of concentric stacked disks. In the uniform distribution, the solute concentration within each disk equaled the Attachment E1 value, and the disk diameter **was** sized to honor the total solute mass for a particular depth. Therefore, the uniform distribution consisted of a series of concentric disks of varying concentration and diameter with depth. The nonuniform distribution comprised of a series of concentric stacked disks of equal diameter. This distribution honored the total solute mass reported in Attachment E1 for the depth, but altered the concentration according to the disk diameter. As the nonuniform distributions were used to investigate concentrating solute mass within the high **flux** regions between tanks, solute concentrations were generally higher than those reported Attachment E1. The displaced distribution was similar to the nonuniform distribution but displaced toward the water table. The alternate distribution was a fixed-diameter distribution that used the **tank** diameters to define the radial extent of solute. The algorithms used to develop variable-diameter and fixed diameter distributions differ and will be described in the sections that follow.

E.2.4.3.1 Variable-Diameter Distribution. The variable-diameter distribution honors both the concentration values and inventory mass at each depth by varying the distribution area as a function of depth. The first step in creating a variable-diameter distribution was to vertically interpolate Attachment E1 values on to the computational grid. The concentration and total solute mass are reported (Attachment E1) at discrete depths or in depth bins for each

combination of tank (i.e., S-104, SX-107, SX-108, SX-109, SX-113, and SX-115) and solute species (i.e., cesium-137, technetium-99, nitrate, and chromium). The cesium-137 data are reported in contiguous depth bins of 9.84 ft for all 6 tanks. The technetium-99, nitrate, and chromium data are reported in disjointed depth bins of 1 ft for tanks SX-107, SX-108, and SX-109 and at discrete depths for tanks S-104, SX-113, and SX-115. Prior to translating to the computational grid, the discrete data were converted into contiguous binned data by using node-centered discretization (i.e., each discrete depth was converted to a depth bin with the discrete depth centered in depth bin). This discretization yielded depth bins that varied in height with elevation.

After converting those data reported as discrete depths to depth bins, the solute concentrations and inventory integrals were translated to the computational grid using an overlapping approach for each combination of tank and solute specie. The computational grids used vertical spacings of 0.4572 m (1.5 ft), compared with the inventory depth bins that varied in height from 0.1524 m (0.5 ft) to 3.7338 m (12.25 ft). For these sets of dimensions, three domain overlapping conditions occurred

- Computational grid totally within the inventory depth bin
- Computational grid partially within the inventory depth bin
- Depth bin totally within the computational grid.

For the first two conditions, a fraction of the inventory in the depth bin was assigned to the grid horizon based on the fraction of overlap. For example, if a 0.4572 m (1.5 ft) grid cell was completely enclosed by a 1.242 m (4.075 ft) depth bin, then 36.81% of the inventory integral would be located in the grid horizon. For the third condition the entire inventory integral for the depth bin would be located in the grid horizon. The overlapping approach, described above, distributes the inventory vertically across the computational domain according to Attachment E1 data and exactly preserves the total inventory for each tank and specie combination.

The horizontal distribution of inventory depended on whether the inventory was variable- or fixed-diameter type. As discussed earlier, the variable-diameter distribution honored both the inventory concentration and total mass reported in Attachment E1, whereas the fixed-diameter distribution only honored the total mass and computed the concentration needed to distribute that inventory mass over a declared region (e.g., the region between two tanks).

The variable-diameter inventory distribution honored both the inventory concentration and total mass at each grid horizon by spreading the inventory over horizon-dependent surface area. When developed the variable-diameter distribution resembles a series of stacked disks of varying diameters, which when translated to two-dimensions resulted in a series of stacked rectangles of varying width but having the same height as in the two-dimensional cross-section.

Note that the inventory concentration was specified as sediment concentrations (e.g., pCi/g) and not as aqueous concentrations. The first step in computing a variable-diameter distribution was to convert the inventory concentration and integral into a surface area, according to Equation E.5.

$$A_{horz}^{3D} = \frac{I_{horz}^{3D}}{C_{horz} z_{horz} \bar{\rho}_b^{3D}{}_{horz}} \quad (E.5)$$

where:

A_{horz}^{3D} = surface area (m²) for the grid horizon (three-dimensional domain)

$\bar{\rho}_b^{3D}{}_{horz}$ = average soil bulk density (kg/m³) for the grid horizon (three-dimensional domain)

I_{horz}^{3D} = total solute mass (Ci or pg) for the grid horizon (three-dimensional domain)

C_{horz} = solute concentration for the grid horizon (Ci/kg soil or µg/kg soil)

z_{horz} = height of the grid horizon (m).

The surface area (three-dimensional domain) was converted to a surface area per unit width for the grid horizon (two-dimensional cross-section) according to Equation E.6.

$$A_{horz}^{2D} = \sqrt{\frac{4 A_{horz}^{3D}}{\pi}} \quad (E.6)$$

where:

A_{horz}^{2D} = surface area per unit width (m²/m) for the grid horizon (two-dimensional cross-section).

Note that 'per unit width' appears because the numerical simulations are based on two-dimensional cross-sectional models.

Assuming that the average soil bulk density for the grid horizon (three-dimensional domain) is equal to that for the two-dimensional cross-section, then the total inventory mass per unit width is computed according to Equation E.7.

$$I_{horz}^{2D} = A_{horz}^{2D} C_{horz} z_{horz} \bar{\rho}_b^{2D}{}_{horz} \quad (E.7)$$

where:

I_{horz}^{2D} = solute inventory per unit width (Ci/m or µg/m) for the grid horizon (two-dimensional cross-section)

$\bar{\rho}_b^{2D}{}_{horz}$ = average soil bulk density (kg/m³) for the grid horizon (two-dimensional cross-section).

To compute number of grid cells (nodes) over which the solute was distributed, the product of the solute concentration for the grid horizon was multiplied by the node length, height, and bulk density and integrated outward from the grid cell that contains the distribution centroid. For each grid horizon, the inventory was distributed over an odd number of grid cells centered on the distribution centroid (e.g., tank centroid). The solute concentration on the two outer grid cells

was adjusted to yield an integrated inventory for the grid horizon that honors the grid-horizon total mass described above. This scheme is expressed mathematically as shown in Equation E.8.

$$I_{horz}^{2D} = \sum_{i=2}^{n-1} C_{horz} \Delta x^i \Delta z^i \rho_b^i + \hat{C} \left[(\Delta x^1 \Delta z^1 \rho_b^1) + (\Delta x^n \Delta z^n \rho_b^n) \right] \quad (E.8)$$

where:

n = odd number of node indices centered around the distribution centroid

Δx = node length (m)

Δz^i = node height (m)

ρ_b^i = node bulk density (kg/m³)

$\hat{C}$ = solute concentration assigned to the two outer most nodes.

The inventory distribution procedure described above worked for cases where the average soil bulk density was known over the distribution area. Because of the heterogeneous nature of the sediments, the average soil bulk density was unknown. Therefore, the actual calculation procedure followed the modified form expressed by Equations E.9 through E.12.

$$\tilde{A}_{horz}^{3D} = \frac{I_{horz}^{3D}}{C_{horz} z_{horz}} \quad (E.9)$$

$$\tilde{A}_{horz}^{2D} = \sqrt{\frac{4 \tilde{A}_{horz}^{3D}}{\pi}} \quad (E.10)$$

$$\tilde{I}_{horz}^{2D} = \tilde{A}_{horz}^{2D} C_{horz} z_{horz} \quad (E.11)$$

$$\tilde{I}_{horz}^{2D} = \sum_{i=2}^{n-1} C_{horz} \Delta x^i \Delta z^i \sqrt{\rho_b^i} + \hat{C} \left[(\Delta x^1 \Delta z^1 \sqrt{\rho_b^1}) + (\Delta x^n \Delta z^n \sqrt{\rho_b^n}) \right] \quad (E.12)$$

where:

$\tilde{A}_{horz}^{3D}$ = surface area per unit bulk density (m²/[kg/m³]) for the grid horizon (three-dimensional domain)

$\tilde{A}_{horz}^{2D}$ = surface area per unit width per unit square root bulk density (m²/m (kg/m³)^{1/2}) for the grid horizon (two-dimensional cross-section)

$\tilde{I}_{horz}^{2D}$ = solute inventory per unit width per unit square root bulk density (Ci/m (kg/m³)^{1/2} or μg/m (kg/m³)^{1/2}) for the grid horizon (two-dimensional cross-section).

E.2.4.3.2 Variable-Diameter Distribution. The fixed-diameter distribution only honors the Attachment E1 inventory total mass at each depth using a declared distribution area. Solute

concentration is computed according to the inventory total mass and distribution area. As with the variable-diameter distribution, the first step in computing the fixed-diameter distribution was to vertically interpolate the Attachment E1 total masses on to the computational grid.

This interpolation procedure was identical to that for the variable-diameter distribution.

The horizontal distribution of inventory was based on the user declared distribution surface area (i.e., radius for a circular distribution) and the inventory total mass for the depth bin.

The concentration within this disk was then computed according to Equation E.13.

$$C_{horz} = \frac{I_{horz}^{3D}}{A_{horz}^{2D} z_{horz} \rho_b^{3D}} \quad (E.13)$$

where:

A_{horz}^{3D} = surface area (m²) for the grid horizon (three-dimensional domain)

ρ_b^{3D} = average soil bulk density (kg/m³) for the grid horizon (three-dimensional domain)

I_{horz}^{3D} = solute inventory (Ci or pg) for the grid horizon (three-dimensional domain)

C_{horz} = solute concentration for the grid horizon (Ci/kg soil or µg/kg soil)

z_{horz} = height of the grid horizon (m).

To determine the number of grid cells over which the inventory was distributed the three-dimensional surface area was converted to a surface area per unit width, according to Equation E.14.

$$A_{horz}^{2D} = \sqrt{\frac{4 A_{horz}^{3D}}{\pi}} \quad (E.14)$$

where:

A_{horz}^{2D} = surface area per unit width (m²/m) for the grid horizon (two-dimensional cross-section).

For each grid horizon, the inventory was distributed over an odd number of grid cells centered on the distribution centroid (e.g., tank centroid) with a length equal to the surface area per unit width. The solute concentrations on the two outer grid cells were adjusted honor the inventory total mass. This scheme is expressed mathematically as shown in Equation E.15.

$$\hat{C} = \frac{I_{horz}^{2D} - \sum_{i=2}^{n-1} C_{horz} \Delta x^i \Delta z^i \rho_b^i}{\left[(\Delta x^1 \Delta z^1 \rho_b^1) + (\Delta x^n \Delta z^n \rho_b^n) \right]} \quad (E.15)$$

where:

n = odd number of node indices centered around the distribution centroid

Δx = node length (m)

Δz^i = node height (m)

ρ_b^i = node bulk density (kg/m³)

$\hat{C}$ = solute concentration assigned to the two outer-most nodes.

E.2.4.3.3 Inventory Distribution Maps. Color-scaled images of the initial inventories, expressed as aqueous concentration for the twelve combinations of solute specie and cross-section, are shown for the uniform distribution in Attachment E2, Figures E2.1 through E2.12, for the nonuniform distribution in Figures E2.13 through E2.24, and for the translated-nonuniform distribution in Figures E2.25 through E2.36, and for the alternate distribution in Figures E2.37 through E2.48. The relationship between initial inventory distribution and simulation cases is shown in Table E. 10.

Simulation Case	Inventory Distribution	Figures*
1	Uniform	E2.1 through E2.12
2	Uniform	E2.1 through E2.12
3	Uniform	E2.1 through E2.12
4	Uniform	E2.1 through E2.12
5	Nonuniform	E2.13 through E2.24
6	Nonuniform	E2.13 through E2.24
7	Displaced nonuniform	E2.25 through E2.36
8	Uniform	E2.1 through E2.12
9	Uniform	E2.1 through E2.12
10	Uniform	E2.1 through E2.12
11	Uniform	E2.1 through E2.12
12	Alternate	E2.37 through E2.48
13	Uniform	E2.1 through E2.12

Specie inventories provided in the modeling data package were expressed in soil concentration (e.g., µg/g soil, pCi/g soil). These concentrations were converted to aqueous-phase concentrations based on the soil bulk density (i.e., from particle density and porosity) and the initial saturation, according to Equation E. 16.

$$C_\ell = \frac{C_s \rho_s (1 - n_T) y_\ell}{s_\ell n_D} \quad (\text{E.16})$$

where:

C_ℓ = aqueous-phase concentration

C_s = soil concentration

ρ_s = soil particle density

n_T = total porosity

y_ℓ = equilibrium fraction of solute in the aqueous phase

s_ℓ = aqueous-phase saturation

n_D = diffusive porosity.

Except for density-dependent Case 8 run, the nitrate solute specie was considered a passive scalar for all simulations; therefore, aqueous-phase properties were independent of its concentration and no precipitation of the solute was considered.

E.3.0 HUMAN HEALTH RISK AND DOSE ESTIMATION APPROACH

This section presents the approach used to estimate human health risk (risk) and dose associated with exposure to contaminants of concern from past leaks and releases from WMA S-SX.

Risk is used herein to refer to the following:

- Incremental lifetime cancer risk (ILCR), which can occur from exposure to carcinogenic chemicals and radionuclides
- Hazard index, which is a measure of the potential for toxic health effects from exposure to noncarcinogenic chemicals.

Dose is the measure of radioactivity potentially received in a human body.

The interim measures under consideration for WMA S-SX address mitigation of groundwater impacts. The exposure pathways for this risk assessment therefore are based on the groundwater exposure medium. The exposure scenarios used for this assessment are as follows:

- Industrial
- Residential
- Industrial worker
- Residential farmer
- Recreational shoreline user.

Risk associated with the use of groundwater from a hypothetical water supply well was estimated at several downgradient points of compliance over a 1,000-year timeframe. Groundwater contaminant concentration estimates were based on the results of the contaminant transport analysis presented in Sections E.4.0 and E.5.0.

The risk assessment for this WMA S-SX field investigation report is qualitative at this stage in the corrective action process even though substantial site-specific data have been generated. Qualitative WMA risk evaluations have been performed at the Hanford Site using historical process and characterization data (**DOE-RL1995c; DOE-RL 1996**). These qualitative risk evaluations have been used to initially evaluate the applicability and relative effectiveness of interim measures (e.g., eliminate leaking water lines and replace well caps). The risk assessment presented herein also relies on historical process and characterization data but is supplemented with additional site-specific data collected under the *Resource Conservation and Recovery Act of 1976* corrective action program as described in Appendices A and B. The results of this risk assessment are used to support evaluation of potential interim measures or interim corrective measures and to determine the need for additional WMA-specific characterization data.

Procedures for the approach and assumptions necessary to calculate human health risk are described in the following:

- “The Model Toxics Control Act Cleanup Regulation” (WAC 173-340), which implements “Model Toxics Control Act” (MTCA) requirements

- **Hanford Site Risk Assessment Methodology** (DOE-RL 1995b; HSRAM), which is the risk assessment methodology that the U.S. Department of Energy (DOE), Washington State Department of Ecology (Ecology), and the U.S. Environmental Protection Agency (EPA) have agreed to use to support Hanford Site cleanup decisions.

The WAC 173-340 implementing regulations define exposure scenarios and input parameters for two types of site uses: unrestricted (MTCA Method B) and industrial (MTCA Method C). Both the Method B and C exposure scenarios include potential consumption of groundwater. The Method B exposure scenario essentially assumes residential use; the scenario has been used in risk assessments of the Hanford Site 100 Areas to represent unrestricted land use (DOE-RL 1995a). The Method C exposure scenario has not been applied for site-specific decisions at the Hanford Site.

Under MTCA, risk assessment requirements for nonradioactive contaminants stipulate that carcinogenic risks shall be less than 10^{-6} (10^{-5} for multiple contaminants) for Method B and 10^{-5} for Method C. Also, concentrations of individual noncarcinogenic contaminants that pose acute or chronic toxic effects to human health shall not exceed a hazard quotient of 1.0. The MTCA risk criteria apply only to nonradioactive contaminants. The EPA guidance indicates that action is generally warranted when the cumulative carcinogenic risk is greater than 10^{-4} or the cumulative noncarcinogenic hazard index exceeds 1.0. Carcinogenic risks below 10^{-6} or hazard indices less than 1.0 are regarded as 'points of departure' below which no action is required. DOE orders require that groundwater protection standards be consistent with federal and Washington State requirements (i.e., EPA and Ecology requirements).

E.3.1 RECEPTOR SCENARIO RATIONALE

Current land use planning assumptions are documented in *Final Hanford Comprehensive Land-Use Plan Environmental Impact Statement* (DOE 1999), which provides an evaluation of several land uses for the Hanford Site for the next 50 years. That environmental impact statement and associated "Hanford Comprehensive Land-Use Plan Environmental Impact Statement (HCP EIS), Hanford Site, Richland, Washington; Record of Decision (ROD)" (64 FR 61615) identify 'industrial-exclusive use' as the planned use for the 200 Areas Central Plateau, an area that encompasses the 200 East and 200 West Areas. Ecology is evaluating how the DOE land-use planning efforts fit within the Ecology cleanup framework. Ecology has not yet agreed to an industrial use scenario. Therefore, multiple exposure scenarios are considered in the WMA S-SX risk assessment to account for the uncertainty of long-term Hanford Site land use.

As shown in *Phase I RCRA Facility Investigation/Corrective Measures Study Work Plan for Single-Shell Tank Waste Management Areas* (DOE-RL 2000), DOE and Ecology have agreed to use MTCA Methods B and C in the corrective action program. MTCA Methods B and C risks are calculated based on equations and parameters specified in the MTCA protocol for establishing groundwater cleanup levels (WAC 173-340-720). Risk is calculated for the residential farmer, industrial worker, and recreational shoreline user exposure scenarios based on the HSRAM. Estimates of risk based on the three HSRAM exposure scenarios are provided in this assessment to allow for comparison to risks cited in *Tank Waste Remediation System, Hanford Site, Richland, Washington, Final Environmental Impact Statement* (DOE and

Ecology 1996; TWRS EIS) and *Retrieval Performance Evaluation Methodology for the AX Tank Farm* (DOE-RL 1999b). Risk calculations for the three HSRAM-based scenarios use groundwater pathway unit risk factors adapted without modification directly from the TWRS EIS.

E.3.1.1 Residential Exposure Scenario (MTCA Method B)

The MTCA cleanup standards are applicable only to nonradioactive constituents. Under the Method B groundwater cleanup level protocol, exposure to hazardous and carcinogenic chemicals is based solely on ingestion of drinking water (with an inhalation correction factor used for volatile chemicals). Method B exposures for noncarcinogenic health effects are based on a drinking water intake rate of 1 L/day (0.2 gal/day) and an average body weight of 16 kg (35 lb) (WAC 173-340-720(3)(a)(ii)(A)). Method B exposures for carcinogenic health effects are based on a drinking water intake rate of 2 L/day (0.5 gal/day), an average body weight of 70 kg (150 lb), an exposure duration of 30 years, and a lifetime of 75 years (WAC 173-340-720(3)(a)(ii)(B)). Oral reference doses (mg/kg-day) and oral slope factors (kg-day/mg) developed by the EPA are applied to convert the exposures to the health effect appropriate for each constituent.

Four hypothetical receptor locations identified by DOE and Ecology (DOE-RL 2000) as the points of compliance for which potential risk will be calculated are as follows:

- Downgradient WMA boundary
 - Downgradient boundary of the 200 West Area
- Downgradient boundary of the 200 Area exclusion zone as defined by the Hanford Future Site Uses Working Group (FSUWG 1992)
- Downgradient at the Columbia River shoreline.

The Method B risk is calculated at all four points of compliance. Note that for the WMA S-SX boundary, risk is calculated at three separate locations corresponding to the three cross-sections (S-CC', SX-DD', SX-FF') considered in the contaminant transport analysis.

E.3.1.2 Industrial Exposure Scenario (MTCA Method C)

As in the MTCA Method B residential exposure scenario, the MTCA Method C industrial exposure scenario is applicable only to nonradioactive constituents. Under the Method C groundwater cleanup level protocol, exposure to hazardous and carcinogenic chemicals is based solely on ingestion of drinking water (with an inhalation correction factor used for volatile chemicals). Method C exposures for noncarcinogenic health effects are based on a drinking water intake rate of 2 L/day (0.5 gal/day) and an average body weight of 70 kg (150 lb) (WAC 173-340-720(4)(b)(ii)(A)). Method C exposures for carcinogenic health effects are based on a drinking water intake rate of 2 L/day (0.5 gal/day), an average body weight of 70 kg (150 lb), an exposure duration of 30 years, and a lifetime of 75 years (WAC 173-340-720(4)(b)(ii)(B)). Oral reference doses (mg/kg-day) and oral slope factors

(kg-day/mg) developed by the EPA are applied to convert the exposures to the health effect appropriate for each constituent.

Method C risk is calculated for the same four points of compliance as defined for the Method B calculations in Section E.3.1.1.

E.3.1.3 Industrial Worker Scenario

An industrial worker scenario consistent with the scenario described in HSRAM is used to represent potential exposure to workers in a commercial or industrial setting. The receptors are adult employees assumed to work at a location for 20 years. A body weight of 70 kg (150 lb) and a lifetime of 70 years are assumed. The scenario involves mainly indoor activities, although outdoor activities (e.g., soil contact) also are included. The groundwater exposure pathways for this scenario include drinking water ingestion (1 L/day [0.2 gal/day]), dermal absorption during showering, shower-water ingestion, and inhalation. These exposures would not be continuous because the worker would go home at the end of each workday (i.e., after 8 hours). The scenario is intended to represent nonremediation workers assumed to wear no protective clothing.

Industrial worker risk is evaluated using a unit risk factor approach consistent with that used for the TWRS EIS and DOE-RL (1999b) analyses. This approach involves calculating risk as the product of the groundwater concentration and the unit risk factor. The basic expression for risk using an unit risk factor approach is:

$$R_{x,y,t} = \sum C_{x,y,t}^i \cdot URF_S^i \quad (\text{E.17})$$

Where:

$R_{x,y,t}$	—	risk at point of compliance x,y,t
$C_{x,y,t}^i$	—	groundwater concentration at point of compliance x,y,t for contaminant i
URF_S^i	=	groundwater unit risk factor for contaminant i and receptor scenario S
x,y	=	horizontal location coordinates
t	—	time.

The summation in Equation E.17 represents addition of the contributions from all constituents. The unit risk factors used for the three HSRAM-based exposure scenarios are shown in Table E. 11. These unit risk factors are for the groundwater pathway and are taken from the risk analysis presented in the TWRS EIS. These unit risk factors were also used in DOE-RL (1999).

Industrial worker risk is calculated for the same four points of compliance as defined in Section E.3.1.1.

Table E.11. Unit Risk Factors for the Industrial Worker, Residential Farmer, and Recreational Shoreline User Scenarios

Contaminant of Concern	Units	Industrial Worker ^a	Residential Farmer ^b	Recreational Shoreline User ^c
C-14	ILCR per Ci/mL	5.23E+06	6.06E+08	8.70E+05
Se-79	ILCR per Ci/mL	3.22E+07	2.87E+08	5.36E+06
Tc-99	ILCR per Ci/mL	7.11E+06	2.61E+08	1.18E+06
			1.29E+10	
Cr	HQ per g/mL	3.31E+06	1.14E+07	3.47E+05
F	HQ per g/mL	1.65E+05	1.61E+06	2.27E+04
Hg	HQ per g/mL	3.85E+07	8.36E+08	4.85E+06
NO ₃	HQ per g/mL	6.20E+03	7.59E+06	8.52E+02
NO ₂	HQ per g/mL	9.92E+03	3.73E+04	1.36E+03
EDTA	HQ per g/mL	7.61E+06	1.47E+09	1.05E+06

E.3.1.4 Residential Farmer Scenario

A residential farmer scenario is used to represent exposures associated with the use of the land for residential and agricultural purposes. This scenario is a slight modification to the residential scenario described in HSRAM; it includes all of the exposure pathways for the residential scenario plus most of the food ingestion pathways described in the HSRAM agriculture scenario. The residential farmer scenario includes using groundwater for drinking water (ingestion rate of 2 L/day [0.5 gal/day]) and other domestic uses as well as for irrigation to produce and consume animals, vegetables, and fruit products. The exposures are assumed to be continuous and include occasional shoreline related recreational activities, which includes contact with surface water sediments. A composite adult is used as the receptor for some of the exposure pathways. The composite adult is evaluated using child parameters for 6 years and adult parameters for 24 years, with total exposure duration of 30 years. Body weights of 16 kg (35 lb) for a child and 70 kg (150 lb) for an adult and a lifetime of 70 years are assumed.

Residential farmer risk is evaluated using a unit risk factor approach as discussed for the industrial worker scenario in Section E.3.1.3. The unit risk factors used are shown in Table E.11.

Residential farmer risks are calculated for the same four points of compliance as defined in Section E.3.1.1.

E.3.1.5 Recreational Shoreline User Scenario

A recreational shoreline user scenario consistent with the scenario described in the HSRAM is used to represent exposure to contamination in groundwater seeps along the Columbia River shoreline from recreational swimming, boating, and other shoreline activities. The scenario involves outdoor activities and occurs only in an area within 400 m (0.25 mi) of the river shoreline. These exposures would not be continuous but would occur for 14 days a year for 30 years. Exposure to both adults and children are taken into account using the same composite adult as described in the residential farmer scenario in Section E.3.1.4.

Recreational shoreline user risk is evaluated using a unit risk factor approach as described in the industrial worker scenario in Section E.3.1.3. The unit risk factors used are shown in Table E.11. Recreational shoreline user risks are calculated only at the downgradient Columbia River shoreline point of compliance that is defined in Section E.3.1.1.

The recreational land user scenario is not included in the WMA S-SX risk assessment because this receptor does not have access to the groundwater pathways.

E.3.2 TANK WASTE CONSTITUENTS OF POTENTIAL CONCERN

Determination of the constituents of potential concern (CoPCs) to be used in the WMA S-SX risk assessment starts with the estimated inventory released from the tank farm system to the environment. That estimated inventory is provided in *Inventory Estimates for SST Leaks in Sand SX Tank Farms* (Jones et al. 2000). The CoPCs listed in the Jones et al. 2000 estimate include the analytes listed in the model cited in *Hanford Defined Wastes: Chemical and Radionuclide Compositions* (Agnew 1997). The following sections provide the rationale used to exclude some of these CoPCs to calculate human health risk and dose in the WMA S-SX risk assessment. Because not all of the constituents associated with the released tank waste will migrate to the groundwater, the contaminants of concern in a groundwater pathway must be selected. The rationale for making this constituents selection is provided in the following sections.

E.3.2.1 Rationale for Excluding Contaminants of Potential Concern

Following are the criteria used to exclude CoPCs from consideration in the WMA S-SX risk assessment.

- Constituents with distribution coefficients (K_d) equal or greater than 0.6. *Composite Analysis for Low-Level Waste disposal in the 200 Area Plateau of the Hanford Site* (Kincaid et al. 1998) provides reference to distribution coefficient selection used in previous studies and for past tank leaks. *Hanford Immobilized Low-Activity Tank Waste Disposal Performance Assessment* (DOE-RL 1999a), along with Kincaid et al. (1998), provides rationale for selection of CoPCs for risk calculations. Numerical modeling results provided in the TWRS EIS indicate that constituents with distribution coefficients equal to or greater than one take over 1,000 years to reach the vadose zone/saturated zone interface. Numerical modeling of past tank leaks for concurrent S tank farm retrieval performance evaluation (Thompson 2001) and for DOE-RL (1999b) indicate that within 1,000 years constituents with distribution coefficients equal to or greater than 0.6 would

not reach the underlying aquifer or would reach the underlying aquifer at very low concentrations (less than 3.0×10^{-2} pCi/L) that would not contribute to significant human health risks (less than 4.0×10^{-8} ILCR for the residential farmer scenario) using base case recharge estimates as shown in Table 3.1.

CoPCs eliminated because of the distribution coefficient criterion are aluminum, iron, bismuth, lanthanum, zirconium, lead, nickel, strontium, manganese, calcium, plutonium (total), nickel-59, nickel-63, cobalt-60, strontium-90, yttrium-90, zirconium-93, niobium-93m, cadmium-113m, antimony-125, tin-126, cesium-134, cesium-137, barium-137, samarium-151, europium-152, europium-154, and europium-155, radium-226, radium-228, plutonium series, americium series, curium series, uranium series, and thorium-232.

- Low-activity radionuclides present in low concentrations and with short half-lives if they have decayed for at least five half-lives. A decay time of 5 half-lives is sufficient for decay of 96.9% of the radionuclide activity and results in a reduced level of potential risk (EPA 1995). Based on numerical modeling results provided in the TWRS EIS, constituents with distribution coefficients of 0 take 150 years to reach the vadose zone/saturated zone interface.

CoPCs eliminated because of the half-life criterion are ruthenium-106 and tritium.

- Constituents without documented human health risk or toxicity factors. The basis for these factors is documented in the *Integrated Risk Information System* (EPA 2000a) or the *User's Guide: Radionuclide Carcinogenicity* (EPA 2000b) databases. A constituent lacking a toxicity reference dose or a carcinogenic slope factor is eliminated.

CoPCs eliminated because of the health effects criterion are carbonate, chloride, calcium, hydroxide, potassium, phosphate, sulfate, silica, and sodium.

Although several organic chemicals are listed in the Agnew (1997) model, only EDTA (ethylenediaminetetraacetic acid) was carried forward because it is the only constituent that has a reference dose. All others were not listed in the Integrated Risk Information System.

In addition, field data was used for revising the risk-producing contaminants of potential concern (Section 3.3.5) that met the criteria in Section 4.3.2.1, but were determined to have inventories associated with below background levels or very small inventories in the vadose zone. The field data assisted in eliminating the uranium series isotopes (see Section 3.3.5) that appears to be overestimated in Jones et al. (2000).

E.3.2.2 Contaminants of Potential Concern for Risk Assessment

The CoPCs to be used in the WMA S-SX risk assessment after applying the exclusion criteria described in Section E.3.2.1 are:

- **Chemicals:** chromium, fluoride, mercury, nitrate, nitrite, and EDTA
- **Radionuclides:** carbon-14; selenium-79; technetium-99; and iodine-129.

E.3.3 ESTIMATING TOTAL INCREMENTAL LIFETIME CANCER RISK AND HAZARD INDEX

The total ILCR for a particular receptor scenario at a particular point in time and space is expressed as the sum of the ILCR calculated for the individual carcinogenic chemical and radionuclide CoPCs. Note that because none of the chemical CoPCs identified in Section E.3.2.2 is classified as carcinogenic, ILCR values for this assessment are based only on radionuclide exposures. Although hexavalent chromium is classified as carcinogenic by inhalation, carcinogenic impacts from hexavalent chromium would apply only for airborne releases from a facility, or for suspension of surface contamination. Because groundwater is the only exposure medium considered in this assessment, neither of these exposure routes applies and hexavalent chromium is treated as an ingestion toxicant. As for the total ILCR, the total hazard index is expressed as the sum of the hazard quotients calculated for the individual noncarcinogenic chemical CoPCs. Total ILCR and hazard index values are calculated for each receptor scenario and point of compliance for the 1,000-year period of analysis used in the contaminant transport simulations.

Risks for CoPCs included in the contaminant transport analysis (i.e., technetium-99, nitrate, and chromium) are based on the modeled groundwater concentrations. Risks for CoPCs not included in the contaminant transport analysis are based on scaled groundwater concentrations. Scaling is performed by multiplying the non-modeled CoPC source inventories (as reported in Jones et al. 2000) by the ratio of the modeled groundwater concentration to source inventory for one of the modeled CoPCs. The basis for the scaling calculations is shown in Table E.12.

Table E.12. Basis for Scaled Groundwater Concentrations

Simulated CoPC	Non-simulated CoPC Ratioed from Simulated CoPC
Tc-99	C-14, Se-79, I-129
Cr	None
NO ₃	NO ₂ , Hg, F, EDTA

E.3.4 DOSE METHODOLOGY

Radionuclide doses are calculated as the product of the groundwater concentration and a unit dose factor. The unit dose factors used are groundwater pathway unit dose factors provided in Kincaid et al. (1998). Unit dose factors are shown in Table E.13. Dose calculations are performed only for the industrial worker exposure scenario. Exposure pathways and parameters associated with this scenario are described in Section E.3.1.3.

Constituent	Unit	Unit Dose Factor
c-14	(mrem/yr)/(pCi/L)	5.22E-04
Se-79	(mrem/yr)/(pCi/L)	2.17E-03
Tc-99	(mrem/yr)/(pCi/L)	3.65E-04
I-129	(mrem/yr)/(pCi/L)	6.90E-02

Industrial worker dose is calculated at the four points of compliance as defined in Section E.3.1.1.

E.4.0 VADOSE ZONE MODELING RESULTS

All simulations reported herein were performed using the STOMP simulator (White and Oostrom 2000a, 2000b). Detailed discussion on the numerical implementation for STOMP and simulation results are presented in *FY00 Initial Assessments for S-SX Field Investigation Report (FIR): Simulations of Contaminant Migration with Surface Barriers* (White et al. 2001). Results presented in the following sections are essentially based on White et al. (2001).

In this section, reporting of modeling results are focused on key flow and transport behavior, mass balance errors, and BTCs at the first compliance point (i.e., WMA S-SX boundary) for the 13 cases for two-dimensional simulations (Section E.2.1). The simulated peak aqueous concentration, time to peak concentration, and the maximum aqueous initial concentration values for the two-dimensional simulations are summarized. The maximum aqueous initial concentration values (based on the inventory estimates in Section E.2.4.3) are presented for comparison with the simulated peak aqueous concentration.

Note that the simulated BTCs and the plume maps for various cases are presented in Attachments E3 and E4, respectively, whereas the results of the recharge sensitivity runs are presented in Attachment E5. Translation of these results to the down-gradient compliance points and streamtube modeling results are described in Section E.5.0. Note that, as a check on the two-dimensional analysis, results of a three-dimensional simulation are presented in this section. However, the risk calculations are all based on two-dimensional simulation results. Also, note that the three cross-sections are labeled in two ways. For example, the row containing tanks SX-107, SX-108, and SX-109 is often labeled as cross-section SX-DD'. Similarly, cross-section SX-FF' refers to the row containing tanks SX-113, SX-114, and SX-115, and cross-section S-CC' refers to the row containing tanks S-104, S-105, and S-106.

E.4.1 BASE CASE, NO ACTION ALTERNATIVE (CASE 1)

The base case suite of simulations, Case 1, investigated solute transport through three cross-sections in WMA S-SX considering natural surface infiltration, with no water-line leaks and no interim surface barriers but with a closure barrier by the year 2040. These simulations were initialized using a steady-flow solution defined by a surface recharge rate of 100 mm/yr and a hydraulic gradient in the unconfined aquifer. Inventories of the four contaminant species were initialized using the uniform distribution pattern. Plot-file output for these simulations was generated at the years 2000, 2010, 2020, 2030, 2040, 2050, 2060, 2070, 2080, 2090, 2100, 2540, and 3000 and include values for the aqueous saturation (θ/θ_s where θ = aqueous moisture content and θ_s = saturated moisture content), aqueous pressure, aqueous moisture content, and concentrations for the four solute species. The moisture content field for these simulations remains unchanged from the initial steady-flow field until the year 2040, when the closure barrier becomes effective.

Solute BTCs at the first compliance point for the three cross-sections (S-CC', SX-DD', and SX-FF') are shown in Attachment E3, Figures E3.1 through E3.9, for the three solute species (technetium-99, chromium, and nitrate), respectively. Aqueous fluxes at the water table for the three cross-sections (S-CC', SX-DD', and SX-FF') are shown in Figures E3.10 through E3.12,

respectively. No cesium-137 was transported to the first compliance point for any of the simulated cross-sections. This is true for Case 1 as well as for all the other simulated cases.

Breakthrough times and aqueous concentrations at the first compliance point are shown in Table E. 14, along with the maximum initial aqueous concentrations. Area-weighted averages (across the three cross-sections) of the solute BTCs were generated for the three solute species and are shown in Attachment E3, Figures E3.13 through E3.15 for technetium-99, chromium, and nitrate, respectively. Comparison of the peak inventory and peak arrival concentrations generally shows an order of magnitude reduction in concentration as the solute migrates through the vadose zone and across the unconfined aquifer within the WMA. Arrival times show a weak dependence on the cross-section geology.

Parameter	s-CC'	SX-DD'	SX-FF'
Arrival Time	2032.9 yr	2050.3 yr	2032.6 yr
Peak Conc.	1.379×10^5 pCi/L	1.233×10^6 pCi/L	2.869×10^7 pCi/L
Max. Initial Conc.'	4.491×10^6 pCi/L	9.480×10^7 pCi/L	5.074×10^6 pCi/L
Arrival Time	2050.3 yr	2053.0 yr	2051.7 yr
Peak Conc.	2.818×10^3 µg/L	1.032×10^5 µg/L	4.538×10^3 µg/L
Max. Initial Conc.	6.456×10^4 µg/L	1.244×10^7 µg/L	1.089×10^5 µg/L
Arrival Time	2032.9 yr	2050.3 yr	2032.9 yr
Peak Conc.	8.461×10^5 µg/L	3.349×10^6 µg/L	1.013×10^6 µg/L
Max. Initial Conc.	3.254×10^7 µg/L	4.448×10^8 µg/L	3.616×10^7 µg/L

Color-scaled images of solute concentrations for the three mobile species (technetium-99, chromium, and nitrate) and three cross-sections (S-CC', SX-DD', and SX-FF') are shown as a series of time sequences in Attachment E4, Figures E4.1 through E4.63. The aqueous concentrations of the solutes are color valued using exponential scaling from the drinking water standard for the specie to the maximum initial inventory concentration, where the standards are 900 pCi/L for technetium-99, 50 µg/L for chromium, and 45,000 µg/L for nitrate. Note the differences in time sequences for cross-section SX-DD' (Figures E4.1 through E4.21); the initial inventory was spread across the region between tanks SX-108 and SX-109 and centered beneath tank SX-107. Although differences are noticeable in the plume located between tanks SX-109 and SX-108 with the plume beneath tank SX-107, the overall rate of migration toward the groundwater is nearly identical. The initial inventory beneath tank SX-107 shows a slight delay in arrival times. The initial inventory distribution for chromium was located beneath the tanks.

The time sequence for chromium, depicted in Figures E4.8 through E4.14, shows an initial upward movement of the solute toward the tank bottoms. This migration occurred, in part, by diffusion, but was additionally aided by the divergent flow of recharge water in the region between tanks at the tank bottom depth. Again, for all cross-sections and solutes, the migration is principally toward the groundwater. Small variations in solute migration direction are noted in cross-section SX-DD' from the sloped gravelly sand strata, but none significantly alter the breakthrough concentrations at the WMA S-SX boundary, located on the lower right-hand corner of the domain.

The aqueous saturation field is dependent on the surface recharge, impermeable structures (e.g., single-shell tanks), various strata and their hydrologic parameters. The steady-flow saturation field for cross-section SX-DD' (tanks SX-107, SX-108, and SX-109) with 100 mm/yr of meteoric recharge is shown in Figure E.8. This field shows the impact of the tanks on the aqueous saturation, where higher than ambient saturations occur above and between the tanks and lower than ambient saturations occur just below the tanks. By 2040 a closure barrier was assumed to be active, which lowered the meteoric recharge from 100 mm/yr to 0.1 mm/yr.

**Figure E.8. Case 1 Aqueous-Phase Saturation at 2000
(steady-flow conditions) for Cross-Section SX-DD'**

The aqueous saturation field dried in response to the change in surface recharge, as shown in Figure E.9 for the year 2050. The impact of the impermeable tanks on the aqueous saturation was reduced at lower surface recharge, as shown by comparing Figures E.8 and E.9. The closure barrier was assumed to remain effective for 500 years, at which point it degrades, allowing meteoric recharge to increase to 3.5 mm/yr. In the 500-year period between 2040 and 2540, the aqueous saturation field continued to slowly dry reaching a minimum average level at 2540, as

shown in Figure E.10. In the 460-year period between 2540 and 3000, the aqueous saturation field wetted, in response to the increased meteoric recharge of 3.5 mm/yr for the degraded surface barrier. The aqueous saturation at year 3000 is shown in Figure E.11. The closure barrier was assumed to decrease the meteoric recharge from 100 mm/yr to 0.1 mm/yr for 500 years and then degrade to 3.5 mm/yr for the next 460 years. These variations in surface recharge had the greatest impact on aqueous saturation in the region between tanks within the backfill material and the soils immediately below the bottom level of the tanks. The Plio-Pleistocene unit soil showed the least change in aqueous saturation with change in the surface recharge. The regions directly beneath the tanks additionally showed lower variability in aqueous saturation.

**Figure E.9. Case 1 Aqueous-Phase Saturation at 2050
(0.1 mm/yr) for Cross-Section SX-DD'**

**Figure E.10. Case 1 Aqueous-Phase Saturation at 2540
(0.1 mm/yr) for Cross-Section SX-DD'**

**Figure E.11. Case 1 Aqueous-Phase Saturation at 3000
(3.5 mm/yr) for Cross-Section SX-DD'**

The water table level showed little variation with the rate of surface recharge; therefore, the mean aqueous saturation in the cross-section gives a general indication of the effect of surface recharge on the hydrologic environment. Mean aqueous phase saturations at selected times during the simulation period are shown in Table E.15 for the three cross-sections (S-CC', SX-DD', and SX-FF'). As expected, the mean saturations follow the trends in surface recharge (i.e., higher mean saturations at higher surface recharge), but the rate of change in mean saturation is slow, as is evidenced by the gradual decrease in saturation during transition from 100 to 0.1 mm/yr in 2040 until the next rate change in 2540. In contrast, the aqueous flow field changes nearly immediately to variations in the surface recharge. The saturation values in Table E.15 show little variation between cross-sections.

Table E.15. Case 1 Mean Aqueous-Phase Saturation

Year	Meteoric Recharge	s-CC'	SX-DD'	SX-FF'
2000	100 mm/yr	0.5481	0.5471	0.5396
2040	100 to 0.1 mm/yr	0.5481	0.5471	0.5396
2050	0.1 mm/yr	0.4987	0.4988	0.4908
2060	0.1 mm/yr	0.4691	0.4962	0.4618
2070	0.1 mm/yr	0.4513	0.4516	0.4445
2080	0.1 mm/yr	0.4393	0.4396	0.4327
2090	0.1 mm/yr	0.4304	0.4307	0.4240
2100	0.1 mm/yr	0.4234	0.4237	0.4172
2540	0.1 to 3.5 mm/yr	0.3625	0.3623	0.3576
3000	35 mm/yr	0.4115	0.4106	0.4060

E.4.2 BARRIER ALTERNATIVE AND NO WATER-LINE LEAKS CASE (CASE 2)

The barrier alternative and no water-line leaks suite of simulations, Case 2, investigated solute transport through three cross-sections in WMA S-SX considering natural surface infiltration, with no water-line leaks and closure barrier by the year 2040. This suite of simulations differs from Case 1 simulations in that an interim surface barrier was implemented between the years 2010 and 2040. These simulations were initialized using a steady-flow solution defined by the surface recharge rate of 100 mm/yr and a hydraulic gradient in the unconfined aquifer. Inventories of the four contaminant species were initialized using the uniform distribution pattern. Plot-file output for these simulations was generated at the years 2000, 2010, 2040, 2540, and 3000 and include values for the aqueous saturation, aqueous pressure, aqueous moisture content, and concentrations for the four solute species. The moisture content field for these simulations remains unchanged from the initial steady-flow.

Solute BTCs at the first compliance point for the three cross-sections (S-CC', SX-DD', and SX-FF') are shown in Attachment E3, Figures E3.16 through E3.24 for the three solute species (technetium-99, chromium, and nitrate), respectively. Aqueous flux at the water table for the three cross-sections (S-CC', SX-DD', and SX-FF') are shown in Figures E3.25 through E3.27, respectively. Breakthrough times and aqueous concentrations at the first compliance point are

shown in Table E.16, along with the maximum initial aqueous concentrations. Area-weighted averages (across the three cross-sections) of the solute BTCs were generated for the three solute species and are shown in Attachment E3, Figures E3.28 through E3.30 for technetium-99, chromium, and nitrate, respectively.

Table E.16. Peak Concentrations and Arrival Times at the First Compliance Point (i.e., WMA S-SX Boundary) for Case 2

Parameter	S-CC'	SX-DD'	SX-FF'
Tc-99			
Arrival Time	2028.3 yr	2059.7 yr	2028.3 yr
Peak Conc.	9.207×10^4 pCi/L	1.839×10^5 pCi/L	2.020×10^5 pCi/L
Max. Initial Conc.'	4.491×10^6 pCi/L	9.480×10^7 pCi/L	5.074×10^6 pCi/L
Arrival Time	2053.3 yr	2072.3 yr	2049.3 yr
Peak Conc.	5.169×10^2 µg/L	9.623×10^3 µg/L	8.621×10^2 µg/L
Max. Initial Conc.	6.456×10^4 µg/L	1.244×10^7 µg/L	1.089×10^5 µg/L
Arrival Time	2028.0 yr	2052.0 yr	2027.7 yr
Peak Conc.	5.739×10^5 µg/L	5.466×10^5 µg/L	6.845×10^5 µg/L
Max. Initial Conc.	3.254×10^7 µg/L	4.448×10^8 µg/L	3.616×10^7 µg/L

Results indicate that the interim surface barrier reduces solute concentrations at the compliance points but has negligible impact on the peak concentration arrival times at the first compliance point. The impact of the interim surface barrier on lower peak concentrations is most effected by the initial inventory distribution. Inventory distributions having concentrations of solute mass nearer the water table were less impacted by the interim barrier compared against the inventory mass located higher in the vadose zone. For example, the technetium-99 inventory for cross-section S-CC' is generally deeper than that for chromium, and the interim barrier reduced its peak concentration by 33%; whereas the reduction in peak concentration for chromium was 82%. Concentrations at the first compliance point at year 3000 were always higher for the interim barrier simulation compared against the Case 1 simulation, which indicates that a major impact of the interim barrier is a smoothing of the breakthrough concentrations at the compliance points.

E.4.3 NO BARRIER AND 25,000 GALLON WATER-LINE LEAK CASE (CASE 3)

The no barrier and 25,000 gallon water-line leak suite of simulations, Case 3, investigated solute transport through one cross-section in the S and SX tank farms considering natural surface infiltration and a closure barrier by the year 2040. This suite of simulations differs from the

Case 1 simulations in that a water-line leak occurs for tank SX-115 in cross-section SX-FF'. The water-line leak was modeled as a point source of water (25,000 gal over a 5-day period) spread over a 15 ft radius between tanks SX-114 and SX-115. The 15 ft radius leak area was translated to the two-dimensional simulation by using a computational grid width of 1 ft and assuming that the center of the circular leak area was situated on the center line between tanks. This approach results in a two-dimensional water-line leak of 1,061 gal over a 5-day period. These simulations were initialized using a steady-flow solution defined by the surface recharge rate of 100 mm/yr and a hydraulic gradient in the unconfined aquifer. Inventories of the four contaminant species were initialized using the uniform distribution pattern. Plot-file output for these simulations was generated at the years 2000, 2000.0137, 2000.0274, 2000.0685, 2000.137, 2000.5, 2001, 2040, 2540, and 3000 and include values for the aqueous saturation, aqueous pressure, aqueous moisture content, and concentrations for the four solute species.

The flow environment following the leak event is shown in a series of color-scaled images of aqueous saturation at 5, 10, 25, 50, 183, and 365 days after the leak in Figures E.12 through E.17, respectively. After 5 days (Figure E.12), the 25,000 gal leak has completely saturated the backfill material between tanks SX-114 and SX-115, with a portion of the saturated zone extending above the tank dome. After 10 days, the leak-water has descended into the undisturbed soils beneath the tanks (Figure E.13), with the peak front sitting above the coarser grained gravelly-sand strata. At 25 and 50 days (Figures E.14 and E.15), the leak has passed through the gravelly-sand strata, continued to migrate downward and diffuse laterally, but showed little migration down the sloped coarser-grained strata. Between 50 days and 1 year, the downward migration of the leak-water plume has slowed (Figures E.16 and E.17), and the aqueous saturation between tanks SX-114 and SX-115 has returned to within a few percent of the steady-flow conditions.

Solute BTCs at the first compliance point for cross-section SX-FF' are shown in Attachment E3, Figures E3.37 through E3.39, for the three solute species (technetium-99, chromium, and nitrate), respectively. Aqueous flux at the water table for cross-section SX-FF' is shown in Figure E3.42. Times and aqueous concentrations for the BTC peaks at the first compliance boundary are shown in Table E.17. Area-weighted averages of the solute BTCs were generated for the three solute species, as shown in Attachment E3, Figures E3.43 through E3.45 for technetium-99, chromium, and nitrate, respectively. These results indicate that although the water-line leak was sufficient to completely saturate the soil between the tanks, it had negligible impact on solute concentration and arrival times at the first compliance point. The rapid dispersion of the saturated water plume beneath the tanks and the homogenizing influence of the Plio-Pleistocene unit were the primary factors influencing the water-line leak.

**Figure E.12. Case 3 Aqueous-Phase Saturation at
2000 plus 5 days for Cross-Section SX-FF'**

**Figure E.13. Case 3 Aqueous-Phase Saturation at
2000 plus 10 days for Cross-Section SX-FF'**

**Figure E.14. Case 3 Aqueous-Phase Saturation at
2000 plus 25 days for Cross-Section SX-FF'**

**Figure E.15. Case 3 Aqueous-Phase Saturation at
2000 plus 50 days for Cross-Section SX-FF'**

**Figure E.16. Case 3 Aqueous-Phase Saturation at
2000 plus 183 days for Cross-Section SX-FF'**

**Figure E.17. Case 3 Aqueous-Phase Saturation at
2000 plus 365 days for Cross-Section SX-FF'**

The impact on the transport of contaminants of the 25,000 gal leak event is shown by comparing the distribution of technetium-99 at 2001 and 2040 (Figures E.18 and E.19). By 2001, the flow field (Figure E.17) has nearly returned to steady-flow conditions leaving the distribution of technetium-99 unaltered from its initial inventory distribution, but for diffusion and reduced concentrations in the region immediately below the tank bottom between tanks SX-114 and SX-115 (Figure E.18). The distribution of technetium-99 in 2040, however, shows general downward migration toward the water table and laterally in the groundwater. These images indicate that the water-line leak event has significantly less impact on the migration of the mobile contaminant than the meteoric recharge over a 40-year period.

Figure E.18. Case 3 Technetium-99 Aqueous Concentration at 2001 for Cross-Section SX-FF'

Figure E.19. Case 3 Technetium-99 Aqueous Concentration at 2040 for Cross-Section SX-FF'

Table E.17. Peak Concentrations and Arrival Times at the First Compliance Point (i.e., WMA S-SX Boundary) for Case 3

Parameter	SX-FF'
Tc-99	
Arrival Time	2031.2 yr
Peak Conc.	2.862×10^5 pCi/L
Max Initial Conc.*	5.074×10^6 pCi/L
Cr	
Arrival Time	2051.3 yr
Peak Conc.	4.565×10^3 µg/L
Max. Initial Conc.	1.089×10^5 µg/L
NO₃	
Arrival Time	2031.9 yr
Peak Conc.	1.018×10^6 µg/L
Max Initial Conc.	3.616×10^7 µg/L

*Maximum initial concentration is based on inventory data (Section E.2.4.3) and listed for comparison with the simulated peak concentration at the compliance boundary.

E.4.4 NO BARRIER AND CLASTIC DIKES CASE (CASE 4)

The no barrier and clastic dikes suite of simulations, Case 4, investigated solute transport through one cross-section in the S and SX tank farms considering natural surface infiltration and a closure barrier by the year 2040. This suite of simulations differs from the Case 1 simulations in that a clastic dike occurs midway between tanks SX-108 and SX-109 in cross-section SX-DD'. The clastic dike was modeled as a vertical feature having hydrologic properties of its infilling material (Table E.4). The computational grid was refined in the horizontal direction in the region around the clastic dike. These simulations were initialized using a steady-flow solution defined by the upper surface recharge rate of 100 mm/yr and a hydraulic gradient in the unconfined aquifer. Inventories of the four contaminant species were initialized using the uniform distribution pattern. Plot-file output for these simulations was generated at the years 2000, 2040, 2540, and 3000 and include values for the aqueous saturation, aqueous pressure, aqueous moisture content, and concentrations for the four solute species.

Solute BTCs at the first compliance point for cross-section SX-DD' are shown in Attachment E3, Figures E3.49 through E3.51 for the three solute species (technetium-99, chromium, and nitrate), respectively. Aqueous flux at the water table for cross-section SX-DD' is shown in Figures E3.56. Times and aqueous concentrations for the BTC peaks at the first compliance boundary are shown in Table E.18. Area-weighted averages of the solute BTCs were generated for the three solute species, as shown in Attachment E3, Figures E3.58 through E3.60 for technetium-99, chromium, and nitrate, respectively. These results indicate that the clastic dike has a negligible impact on solute peak concentrations and arrival times at the first compliance point. This result is due in part to the location of the clastic dike outside of initial inventory distribution and the negligible impact of the dike on the response of the flow system.

Table E.18. Peak Concentrations and Arrival Times at the First Compliance Point (i.e., WMA S-SX Boundary) for Case 4

Parameter	SX-DD'
Arrival Time	2050.3 yr
Peak Conc.	1.227×10^6 pCi/L
Max Initial Conc.	9.480×10^7 pCi/L
Cr	
Arrival Time	2053.3 yr
Peak Conc.	1.022×10^5 µg/L
Max initial Conc.	1.244×10^7 µg/L
NO ₃	
Amval Time	2050.7 yr
Peak Conc.	3.320×10^6 µg/L
Max Initial Conc.	4.448×10^8 µg/L

E.4.5 NONUNIFORM INVENTORY DISTRIBUTION AND NO BARRIER CASE (CASE 5)

The nonuniform inventory distribution and no barrier suite of simulations, Case 5, investigated solute transport through three cross-sections in the S and SX tank farms considering natural surface infiltration, with no water-line leaks and closure barrier by the year 2040. This suite of simulations differs from the Case 1 simulations in that a nonuniform distribution was used for the initial inventory; where the inventory distribution by depth was maintained, but concentrated between tanks (Section E.2.4.2.2). These simulations were initialized using a steady-flow solution defined by the surface recharge rate of 100 mm/yr and a hydraulic gradient in the unconfined aquifer. Inventories of the four contaminant species were initialized using the nonuniform distribution pattern. Plot-file output for these simulations was generated at the years 2000, 2010, 2040, 2540, and 3000 and include values for the aqueous saturation, aqueous pressure, aqueous moisture content, and concentrations for the four solute species. The moisture content field for these simulations remains unchanged from the initial steady-flow field until the year 2040, when the closure barrier becomes effective.

Solute BTCs at the first compliance point for the three cross-sections (S-CC', SX-DD', and SX-FF') are shown in Attachment E3, Figures E3.61 through E3.69 for the three solute species (technetium-99, chromium, and nitrate), respectively. Aqueous flux at the water table for the three cross-sections (S-CC', SX-DD', and SX-FF') are shown in Figures E3.70 through E3.72, respectively. Times and aqueous concentrations for the BTC peaks at the first compliance boundary are shown in Table E.19. Area-weighted averages (across the three cross-sections) of the solute BTCs were generated for the three solute species and are shown in Attachment E3, Figures E3.73 through E3.75 for technetium-99, chromium, and nitrate, respectively.

Parameter	S-CC'	SX-DD'	SX-FF'
Arrival Time	2031.9 yr	2048.7 yr	2030.9 yr
Peak Conc.	1.779×10^6 pCi/L	5.428×10^6 pCi/L	2.627×10^6 pCi/L
Max Initial Conc.*	6.262×10^8 pCi/L	2.033×10^9 pCi/L	4.425×10^8 pCi/L
Cr			
Arrival Time	2050.3 yr	2051.3 yr	2049.3 yr
Peak Conc.	3.872×10^4 µg/L	4.485×10^5 µg/L	3.615×10^4 µg/L
Max. Initial Conc.	1.710×10^7 µg/L	1.074×10^8 µg/L	7.290×10^6 µg/L
NO₃			
Arrival Time	2031.6 yr	2049.0 yr	2029.6 yr
Peak Conc.	7.915×10^6 µg/L	7.635×10^6 µg/L	4.382×10^6 µg/L
Max. Initial Conc.	2.711×10^9 µg/L	2.159×10^9 µg/L	7.048×10^8 µg/L

As indicated by the figures and Table E. 19, the nonuniform distribution of initial inventory has negligible impact on arrival times of peak concentrations at the WMA S-SX boundary. This result agrees with other observations, in that peak arrival times at the WMA S-SX boundary were most strongly correlated with the initial depth of the peak concentration. The nonuniform distribution had initial aqueous concentrations that were between 4.85 and 264 times greater than corresponding values for the uniform distribution; whereas, the resulting peak concentrations at the WMA S-SX boundary were only 2.27 to 13.7 times greater than the corresponding values for the uniform distribution. The nonuniform distribution, therefore, resulted in greater dilution of the contaminant concentrations in migrating to the first compliance point from the initial inventory distribution.

E.4.6 NONUNIFORM INVENTORY DISTRIBUTION AND BARRIER CASE (CASE 6)

The nonuniform inventory distribution and barrier suite of simulations, Case 6, investigated solute transport through three cross-sections in the S and SX tank farms considering natural surface infiltration, an interim barrier, with no water-line leaks and closure barrier by the year 2040. This suite of simulations differs from the Case 1 simulations in that an interim surface barrier was implemented between the years 2010 and 2400, and a nonuniform distribution was used for the initial inventory; where the inventory distribution by depth was maintained, but concentrated between tanks (Section E.2.4.2.2). These simulations were initialized using a steady-flow solution defined by the upper surface recharge rate of 100 mm/yr and a hydraulic gradient in the unconfined aquifer. Inventories of the four contaminant species were initialized using the uniform distribution pattern. Plot-file output for these simulations was generated at the years 2000, 2010, 2040, 2540, and 3000 and include values for the aqueous saturation, aqueous pressure, aqueous moisture content, and concentrations for the four solute species. The moisture content field for these simulations remains unchanged from the initial steady-flow field until the year 2010, when the interim barrier becomes effective.

Solute BTCs at the first compliance point for the three cross-sections (S-CC', SX-DD', and SX-FF') are shown in Attachment E3, Figures E3.76 through E3.84, for the three solute species (technetium-99, Chromium, and nitrate), respectively. Aqueous **flux** at the water table for the three cross-sections (S-CC', SX-DD', and SX-FF') are shown in Figures E3.85 through E3.87, respectively. Times and aqueous concentrations for the BTC peaks at the first compliance boundary are shown in Table E.20. Area-weighted averages (across the three cross-sections) of the solute BTCs were generated for the three solute species, as shown in Attachment E3, Figures E3.88 through E3.90 for technetium-99, chromium, and nitrate, respectively. Compared against the simulations for the nonuniform inventory distribution and no interim barrier case (Case 5), these results reflect those found for uniform inventory distributions with and without an interim barrier. As expected, the interim barrier has the greatest impact on reducing peak concentrations at the WMA S-SX boundary for those inventory distributions with solute mass located higher in the vadose zone (i.e., chromium).

Table E.20. Peak Concentrations and Arrival Times at the First Compliance Point (i.e., WMA S-SX Boundary) for Case 6

Parameter	S-CC'	SX-DD'	SX-FF'
Arrival Time	2027.7 yr	2054.7 yr	2027.3 yr
Peak Conc.	1.236×10^6 pCi/L	8.669×10^5 pCi/L	2.000×10^6 pCi/L
Max. Initial Conc.'	6.262×10^8 pCi/L	2.033×10^9 pCi/L	4.425×10^8 pCi/L
	Cr		
Arrival Time	2050.3 yr	2063.0 yr	2044.0 yr
Peak Conc.	6.607×10^3 µg/L	4.786×10^4 µg/L	7.732×10^3 µg/L
Max. Initial Conc.	1.710×10^1 µg/L	1.074×10^8 µg/L	7.290×10^6 µg/L
Arrival Time	2027.3 yr	2050.0 yr	2026.0 yr
Peak Conc.	5.648×10^6 µg/L	1.291×10^6 µg/L	3.339×10^6 µg/L
Max. Initial Conc.	2.711×10^9 µg/L	2.159×10^9 µg/L	7.048×10^8 µg/L

E.4.7 LOCATION OF INVENTORY DISTRIBUTION AND NO BARRIER CASE (CASE 7)

The location of inventory distribution and no barrier suite of simulations, Case 7, investigated solute transport through three cross-sections in the S and SX tank farms considering natural surface infiltration, with no water-line leaks and closure barrier by the year 2040, and an inventory location close to the water table. This suite of simulations differs from the Case 1 simulations in that a displaced-nonuniform distribution was used for the initial inventory; where the inventory distribution by depth was maintained, but concentrated between tanks and shifted toward the water table (Section E.2.4.2.3). These simulations were initialized using a steady-flow solution defined by the upper surface recharge rate of 100mm/yr and a hydraulic gradient in the unconfined aquifer. Plot-file output for these simulations was generated at the years 2000, 2010, 2040, 2540, and 3000 and include values for the aqueous saturation, aqueous pressure, aqueous moisture content, and concentrations for the four solute species. The moisture content field for these simulations remains unchanged from the initial steady-flow field until the year 2040, when the closure barrier becomes effective.

Solute BTCs at the first compliance point for the three cross-sections (S-CC', SX-DD', and SX-FF') are shown in Attachment E3, Figures E3.91 through E3.99, for the three solute species (technetium-99, chromium, and nitrate), respectively. Aqueous flux at the water table for the three cross-sections (S-CC', SX-DD', and SX-FF') are shown in Attachment E3, Figures E3.100 through E3.102, respectively. Times and aqueous concentrations for the BTC peaks at the first compliance boundary are shown in Table E.21. Area-weighted averages (across the three

cross-sections) of the solute BTCs were generated for the three solute species and are shown in Attachment E3, Figures E3.103 through E3.105 for technetium-99, chromium, and nitrate, respectively. These results indicate that locating the inventory near the water table greatly influences solute transport to the first compliance point, yielding earlier peak arrival times and higher peak concentrations. For cross-section S-CC', compared with the uniform distribution (Case 1), peak concentrations at the first compliance point, due to the displaced-nonuniform distribution, were 23.6 to 41.7 times higher, depending on the solute. The corresponding factors varied from 4.61 to 9.40 for cross-section SX-DD' and 12.9 to 25.4 for cross-section SX-FF', depending on the solute.

Parameter	s-CC'	SX-DD'	SX-FF'
Arrival Time	2006.9 yr	2014.9 yr	2007.6 yr
Peak Conc.	5.754×10^6 pCi/L	1.159×10^7 pCi/L	7.285×10^6 pCi/L
Max. Initial Conc.'	6.262×10^8 pCi/L	2.033×10^9 pCi/L	4.425×10^8 pCi/L
Cr			
Arrival Time	2014.6 yr	2019.6 yr	2014.3 yr
Peak Conc.	6.640×10^4 µg/L	7.633×10^5 µg/L	6.372×10^4 µg/L
Max. Initial Conc.	1.710×10^7 µg/L	1.074×10^8 µg/L	7.290×10^6 µg/L
Arrival Time	2006.6 yr	2014.9 yr	2005.9 yr
Peak Conc.	2.447×10^7 µg/L	1.545×10^7 µg/L	1.310×10^7 µg/L
Max. Initial Conc.	2.711×10^9 µg/L	2.159×10^9 µg/L	7.048×10^8 µg/L

the simulated peak concentration at the compliance boundary.

E.4.8 DENSITY AND VISCOSITY EFFECTS CASE (CASE 8)

The density and viscosity effects suite of simulations, Case 8, investigated solute transport through three cross-sections in the S and SX tank farms considering natural surface infiltration, with no water-line leaks and closure barrier by the year 2040. This suite of simulations differs from the Case 1 simulations in that the aqueous phase density and viscosity were dependent on the nitrate concentration, as described in Section E.2.2.5. These simulations were initialized using a steady-flow solution defined by the surface recharge rate of 100mm/yr and a hydraulic gradient in the unconfined aquifer. Inventories of the four contaminant species were initialized using the uniform distribution pattern. Plot-file output for these simulations was generated at the years 2000, 2010, 2040, 2540, and 3000 and include values for the aqueous saturation, aqueous pressure, aqueous moisture content, and concentrations for the four solute species.

Solute BTCs at the first compliance point for the three cross-sections (S-CC', SX-DD', and SX-FF') are shown in Attachment E3, Figures E3.106 through E3.114 for the three solute species (technetium-99, chromium, and nitrate), respectively. Aqueous **flux** at the water table for the three cross-sections (S-CC', SX-DD', and SX-FF') are shown in Figures E3.115 through E3.117, respectively. Times and aqueous concentrations for the BTC peaks at the first compliance boundary are shown in Table E.22. Area-weighted averages (across the three cross-sections) of the solute BTCs were generated for the three solute species and are shown in Attachment E3, Figures E3.118 through E3.120 for technetium-99, chromium, and nitrate, respectively.

Parameter	S-CC'	SX-DD'	SX-FF'
Arrival Time	2032.7 yr	2050.0 yr	2032.3 yr
Peak Conc.	1.393×10^5 pCi/L	1.260×10^6 pCi/L	2.905×10^5 pCi/L
Max. Initial Conc.'	4.491×10^6 pCi/L	9.480×10^7 pCi/L	5.074×10^6 pCi/L
Arrival Time	2050.3 yr	2052.3 yr	2051.3 yr
Peak Conc.	2.819×10^3 µg/L	1.052×10^5 µg/L	4.545×10^3 µg/L
Max. Initial Conc.	6.456×10^4 µg/L	1.244×10^7 µg/L	1.089×10^5 µg/L
NO₃			
Arrival Time	2032.7 yr	2050.0 yr	2032.3 yr
Peak Conc.	8.538×10^7 µg/L	3.423×10^6 µg/L	1.024×10^6 µg/L
Max. Initial Conc.	3.254×10^7 µg/L	4.448×10^8 µg/L	3.616×10^7 µg/L

Increasing nitrate concentration increases both the aqueous density and viscosity. These property changes have opposite effect; that is, increasing aqueous density increases the gravitational body force on a nitrate plume, but increasing viscosity reduces the plume fluidity. Because of the opposing flow effects, the solute migration toward the WMA S-SX boundary was nearly unchanged from the Case 1 simulations.

E.4.9 BASE CASE WITH 50 MM/YR METEORIC RECHARGE CASE (CASE 9)

The base case with 50 mm/yr meteoric recharge suite of simulations, Case 9, investigated solute transport through three cross-sections in WMA S-SX considering natural surface infiltration, with no water-line leaks and no interim surface barriers, but with a closure barrier by the year 2040. These simulations along with those from Cases 1, 10, and 11 form a sensitivity study on the effect of meteoric recharge on the migration of solutes to the WMA S-SX boundary.

The simulations in this case were initialized using a steady-flow solution defined by the surface recharge rate of 50 mm/yr and a hydraulic gradient in the unconfined aquifer. Inventories of the four contaminant species were initialized using the uniform distribution pattern. Plot-file output for these simulations was generated at the years 2000, 2040, 2540, and 3000 and include values for the aqueous saturation, aqueous pressure, aqueous moisture content, and concentrations for the four solute species. The moisture field for these simulations remains unchanged from the initial steady-flow field until the year 2040, when the closure barrier becomes effective.

Solute BTCs at the first compliance point for the three cross-sections (S-CC', SX-DD', and SX-FF') are shown in Attachment E3, Figures E3.121 through E3.129, for the three solute species (technetium-99, chromium, and nitrate), respectively. Aqueous fluxes at the water table for the three cross-sections (S-CC', SX-DD', and SX-FF') are shown in Figures E3.130 through E3.132, respectively. Breakthrough times and aqueous concentrations at the first compliance point are shown in Table E.23, along with the maximum initial aqueous concentrations. Area-weighted averages (across the three cross-sections) of the solute BTCs were generated for the three solute species and are shown in Attachment E3, Figures E3.133 through E3.135 for technetium-99, chromium, and nitrate, respectively.

Parameter	s-CC'	SX-DD'	SX-FF'
Arrival Time	2055.9 yr	2074.0 yr	2054.3 yr
Peak Conc.	9.234×10^4 pCi/L	3.744×10^5 pCi/L	1.988×10^5 pCi/L
Max. Initial Conc.'	4.491×10^6 pCi/L	9.480×10^7 pCi/L	5.074×10^6 pCi/L
Anival Time	2072.3 yr	2081.7 yr	2070.3 yr
Peak Conc.	8.966×10^2 µg/L	2.221×10^4 µg/L	1.651×10^3 µg/L
Max. Initial Conc.	6.456×10^4 µg/L	1.244×10^7 µg/L	1.089×10^5 µg/L
NO₃			
Arrival Time	2055.3 yr	2071.3 yr	2054.0 yr
Peak Conc.	5.688×10^5 µg/L	1.048×10^6 µg/L	7.135×10^5 µg/L
Max. Initial Conc.	3.254×10^7 µg/L	4.448×10^8 µg/L	3.616×10^7 µg/L

The steady-flow saturation field for cross-section SX-DD' (tanks SX-107, SX-108, and SX-109) with 50 mm/yr of meteoric recharge is shown in Figure E.20. This field shows little variation from that for the 100 mm/yr meteoric recharge case (Case 1) (Figure E.8). Although this series of simulations yielded only slight changes in the initial mean saturation (Tables E.15 and E.24), peak concentrations and their arrival times at the WMA S-SX boundary changed considerably.

Reductions in solute concentrations at the WMA S-SX boundary were primarily correlated with the initial inventory distributions. The technetium-99 and nitrate solute concentrations were reduced to approximately 60% of the Case 1 values; whereas, the chromium solute concentrations showed reductions to approximately 30%. Comparisons of solute BTCs for the various initial meteoric recharge rates at the first compliance point are shown for each combination of cross-section and solute in Attachment E5, Figures E5.1 through E5.9. Comparisons of aqueous fluxes at the water table for the various initial meteoric recharge rates for the three cross-sections are shown in Figures E5.10 through E5.12.

Figure E.20. Case 9 Aqueous-Phase Saturation at 2000 (50 mm/yr) for Cross-Section SX-DD'

Table E.24. Case 9 Mean Aqueous-Phase Saturation

Year	Meteoric Recharge	S-CC'	SX-DD'	SX-FF'
2000	50 mm/yr	0.5135	0.5125	0.5057
2040	50 to 0.1 mm/yr	0.5135	0.5125	0.5057
2540	0.1 to 3.5 mm/yr	0.3625	0.3623	0.3576
3000	3.5 mm/yr	0.4115	0.4106	0.4060

The water table level showed little variation with the rate of surface recharge; therefore, the mean aqueous saturation in the cross-section gives a general indication of the effect of surface recharge on the flow environment. Mean aqueous phase saturations at selected times during the simulation period are shown in Table E.24 for the three cross-sections (S-CC', SX-DD', and SX-FF'). As expected, the mean saturations follow the trends in surface recharge (i.e., higher mean saturations at higher surface recharge). However, the rate of change in mean saturation is slow, as evidenced by the gradual decrease in saturation during transition from 50 to 0.1 mm/yr in 2040 until the next rate change in 2540. In contrast, the aqueous flow field changes almost immediately to variations in the surface recharge. The saturation values in Table E.24 show little variation between cross-sections.

E.4.10 BASE CASE WITH 30 MM/YR METEORIC RECHARGE (CASE 10)

The base case with 30 mm/yr meteoric recharge suite of simulations, Case 10, investigated solute transport through three cross-sections in WMA S-SX considering natural surface infiltration, with no water-line leaks and no interim surface barriers, but with a closure barrier by the year 2040. These simulations along with those from Cases 1, 9, and 11 form a sensitivity study on the effect of meteoric recharge on the migration of solutes to the WMA S-SX boundary.

The simulations in this case were initialized using a steady-flow solution defined by the surface recharge rate of 30 mm/yr and a hydraulic gradient in the unconfined aquifer. Inventories of the four contaminant species were initialized using the uniform distribution pattern. Plot-file output for these simulations was generated at the years 2000, 2040, 2540, and 3000 and include values for the aqueous saturation, aqueous pressure, aqueous moisture content, and concentrations for the four solute species. The moisture content field for these simulations remains unchanged from the initial steady-flow field until the year 2040, when the closure barrier becomes effective.

Solute BTCs at the first compliance point for the three cross-sections (S-CC', SX-DD', and SX-FF') are shown in Attachment E3, Figures E3.136 through E3.144, for the three solute species (technetium-99, chromium, and nitrate), respectively. Aqueous fluxes at the water table for the three cross-sections (S-CC', SX-DD', and SX-FF') are shown in Figures E3.145 through E3.147, respectively. Breakthrough times and aqueous concentrations at the first compliance point are shown in Table E.25, along with the maximum initial aqueous concentrations. Area-weighted averages (across the three cross-sections) of the solute BTCs were generated for the three solute species and are shown in Attachment E3, Figures E3.148 through E3.150 for technetium-99, chromium, and nitrate, respectively.

Table E.25. Peak Concentrations and Arrival Times at the First Compliance Point (i.e., WMA S-SX Boundary) for Case 10

Parameter	s-CC'	SX-DD'	SX-FF'
Arrival Time	2073.0 yr	2125.3 yr	2070.3 yr
Peak Conc.	5.219×10^4 pCi/L	1.114×10^5 pCi/L	1.233×10^5 pCi/L
Max. Initial conc.'	4.491×10^6 pCi/L	9.480×10^7 pCi/L	5.074×10^6 pCi/L
Arrival Time	2115.3 yr	3000.0 yr	2070.3 yr
Peak Conc.	3.013×10^2 µg/L	7.248×10^3 µg/L	5.903×10^2 µg/L
Max. Initial Conc.	6.456×10^4 µg/L	1.244×10^5 µg/L	1.089×10^5 µg/L
Arrival Time	2072.3 yr	2113.0 yr	2070.0 yr
Peak Conc.	3.268×10^5 µg/L	3.240×10^5 µg/L	4.324×10^5 µg/L
Max. Initial Conc.	3.254×10^7 µg/L	4.448×10^8 µg/L	3.616×10^7 µg/L

The steady-flow saturation field for cross-section **SX-DD'** (tanks **SX-107**, **SX-108**, and **SX-109**) with **30 mm/yr** of meteoric recharge is shown in Figure E.21. The saturation field shows slight variation from those for the **50 mm/yr** (Case 9) and **100 mm/yr** (Case 1) meteoric recharge cases (Figures E.8 and E.20). Most notable is the overall reduction in saturation and the reduction in shadowing beneath the tanks. The effects of lowering the initial meteoric recharge to 30 mm/yr were similar to those of lowering the recharge from 100 to 50 mm/yr; peak concentrations at the WMA S-SX boundary were lowered and arrival times of the concentration peaks were delayed. Again, reductions in solute concentrations at the WMA S-SX boundary were primarily correlated with the initial inventory distributions. Comparisons of solute BTCs for the four initial meteoric recharge rates (100, 50, 30, and 10 mm/yr) at the first compliance point are shown for each combination of cross-section and solute in Attachment E5, Figures E5.1 through E5.9. Likewise, comparisons of aqueous fluxes at the water table for the four initial meteoric recharge rates for the three cross-sections are shown in Figures E5.10 through E5.12.

Figure E.21. Case 10 Aqueous-Phase Saturation at 2000 (30 mm/yr) for Cross-Section SX-DD'

The water table level showed little variation with the rate of surface recharge; therefore, the mean aqueous saturation in the cross-section gives a general indication of the effect of surface recharge on the hydrologic environment. Mean aqueous phase saturations at selected times during the simulation period are shown in Table E.26 for the three cross-sections (S-CC', SX-DD', and SX-FF'). The saturation values in Table E.26 show little variation between cross-sections.

Table E.26. Case 10 Mean Aqueous-Phase Saturation

Year	Meteoric Recharge	s-CC'	SX-DD'	SX-FF'
2000	30 mm/yr	0.4902	0.4893	0.4829
2040	30 to 0.1 mm/yr	0.4902	0.4893	0.4829
2540	0.1 to 3.5 mm/yr	0.3625	0.3623	0.3576
3000	3.5 mm/yr	0.4115	0.4106	0.4060

E.4.11 BASE CASE WITH 10 MMNR METEORIC RECHARGE (CASE 11)

The base case with 10 mm/yr meteoric recharge suite of simulations, Case 11, investigated solute transport through three cross-sections in the WMA S-SX considering natural surface infiltration, with no water-line leaks and no interim surface barriers, but with a closure barrier by the year 2040. These simulations along with those from Cases 1, 9, and 10 form a sensitivity study on the

effect of meteoric recharge on the migration of solutes to the WMA S-SX boundary.

The simulations in this case were initialized using a steady-flow solution defined by the surface recharge rate of 10mm/yr and a hydraulic gradient in the unconfined aquifer. Inventories of the four contaminant species were initialized using the uniform distribution pattern. Plot-file output for these simulations was generated at the years 2000,2040,2540, and 3000 and include values for the aqueous saturation, aqueous pressure, aqueous moisture content, and concentrations for the four solute species. The moisture content field for these simulations remains unchanged from the initial steady-flow field until the year 2040, when the closure barrier becomes effective.

Solute BTCs at the first compliance point for the three cross-sections (S-CC', SX-DD', and SX-FF') are shown in Attachment E3, Figures E3.151 through E3.159, for the three solute species (technetium-99, chromium, and nitrate), respectively. Aqueous fluxes at the water table for the three cross-sections (S-CC', SX-DD', and SX-FF') are shown in Figures E3.160 through E3.162, respectively. Breakthrough times and aqueous concentrations at the first compliance point are shown in Table E.27, along with the maximum initial aqueous concentrations. Area-weighted averages (across the three cross-sections) of the solute BTCs were generated for the three solute species and are shown in Attachment E3, Figures E3.163 through E3.165 for technetium-99, chromium, and nitrate, respectively.

Table E.27. Peak Concentrations and Arrival Times at the First Compliance Point (i.e., WMA S-SX Boundary) for Case 11

Parameter	S-CC'	SX-DD'	SX-FF'
Tc-99			
Arrival Time	2176.0 yr	3000.0 yr	2153.0 yr
Peak Conc.	1.057×10^4 pCi/L	6.775×10^4 pCi/L	2.783×10^4 pCi/L
Max. Initial Conc.*	4.491×10^6 pCi/L	9.480×10^7 pCi/L	5.074×10^6 pCi/L
Cr			
Arrival Time	3000.0 yr	3000.0 yr	3000.0 yr
Peak Conc.	1.609×10^2 µg/L	4.157×10^3 µg/L	3.133×10^2 µg/L
Max. Initial Conc.	6.456×10^4 µg/L	1.244×10^7 µg/L	1.089×10^5 µg/L
Nitrate			
Arrival Time	2171.0 yr	3000.0 yr	2152.0 yr
Peak Conc.	6.819×10^4 µg/L	1.812×10^5 µg/L	9.895×10^4 µg/L
Max. Initial Conc.	3.254×10^7 µg/L	4.448×10^8 µg/L	3.616×10^7 µg/L

*Maximum initial concentration is based on inventory data (Section E.2.4.3) and listed for comparison with the simulated peak concentration at the compliance boundary.

The steady-flow saturation field for cross-section SX-DD' (tanks SX-107, SX-108, and SX-109) with 10mm/yr of meteoric recharge is shown in Figure E.22. Compared against the steady-flow saturation fields for 100, 50, and 30 mm/yr (Figures E.8, E.20, and E.21), the saturation field at 10mm/yr shows no shadowing from the tanks and only slight increases in moisture between the

tanks. The 10 mm/yr recharge rate differs from the higher recharge rates investigated; the downward aqueous flow was sufficiently low to delay the peak arrival times to after the year 3000 for those solutes with shallower initial inventories. This behavior was predicted for chromium in all three cross-sections, and for technetium-99 and nitrate in cross-section SX-DD. In general, the solute transport response to lower meteoric recharge is similar to that for surface barriers, but with greater consequence because of the earlier implementation of the reduced migration rates toward the groundwater. Comparisons of solute BTCs for the four initial meteoric recharge rates (100, 50, 30, and 10 mm/yr) at the first compliance point are shown for each combination of cross-section and solute in Attachment E5, Figures E5.1 through E5.9. Comparison of aqueous fluxes at the water table for the four initial meteoric recharge rates for the three cross-sections are shown in Figures E5.10 through E5.12.

Figure E.22. Case 11 Aqueous-Phase Saturation at 2000 (50 mm/yr) for Cross-Section SX-DD'

The water table level showed little variation with the rate of surface recharge; therefore, the mean aqueous saturation in the cross-section gives a general indication of the effect of surface recharge on the hydrologic environment. Mean aqueous phase saturations at selected times during the simulation period are shown in Table E.28 for the three cross-sections (S-CC', SX-DD', and SX-FF'). As expected the mean saturations follow the trends in surface recharge (i.e., higher mean saturations at higher surface recharge). The saturation values in Table E.28 show little variation between cross-sections.

Year	Meteoric Recharge	S-CC'	SX-DD'	SX-FF'
2000	50 mm/yr	0.4463	0.4455	0.4108
2040	50 to 0.1 mm/yr	0.4463	0.4455	0.4108
2540	0.1 to 3.5 mm/yr	0.3625	0.3623	0.3576
3000	3.5 mm/yr	0.4115	0.4106	0.4060

E.4.12 ALTERNATE INVENTORY DISTRIBUTION CASE (CASE 12)

The alternate inventory distribution suite of simulations, Case 12, investigated solute transport through three cross-sections in WMA S-SX considering natural surface infiltration, with no water-line leaks and closure barrier by the year 2040, and an alternate nonuniform distribution. The alternate inventory distributions are shown in Attachment E2, Figures E2.37 through E2.48. This suite of simulations differs from the Case 1 simulations in that an alternate distribution was used for the initial inventory; where the inventory distribution by depth was maintained but uniformly spread over the region beneath the tanks. These simulations were initialized using a steady-flow solution defined by the surface recharge rate of 100 mm/yr and a hydraulic gradient in the unconfined aquifer. Plot-file output for these simulations was generated at the years 2000, 2010, 2040, 2540, and 3000 and include values for the aqueous saturation, aqueous pressure, aqueous moisture content, and concentrations for the four solute species. The moisture content field for these simulations remains unchanged from the initial steady-flow field until the year 2040, when the closure barrier becomes effective. This set of simulations was performed to investigate the sensitivity of the Case 1 results to moderate variations in the inventory distribution.

Solute BTCs at the first compliance point for the three cross-sections (S-CC', SX-DD', and SX-FF') are shown in Attachment E3, Figures E3.166 through E3.174 for the three solute species (technetium-99, chromium, and nitrate), respectively. Aqueous flux at the water table for the three cross-sections (S-CC', SX-DD', and SX-FF') are shown in Figures E3.175 through E3.177, respectively. Times and aqueous concentrations for the BTC peaks at the first compliance boundary are shown in Table E.29. Area-weighted averages (across the three cross-sections) of the solute BTCs were generated for the three solute species, as shown in Attachment E3, Figures E3.178 through E3.180 for technetium-99, chromium, and nitrate, respectively. When peak arrival concentration was weighted by maximum initial concentration, the breakthrough concentrations of the alternate distribution varied from those for the uniform distribution (i.e., Case 1 simulation) by 9.7 to 81.6%, depending on the solute. The results provide an indication of variations in peak arrival concentrations with uncertainty in the areal location of the initial inventory.

Table E.29. Peak Concentrations and Arrival Times at the First Compliance Point (i.e., WMA S-SX Boundary) for Case 12

Parameter	S-CC'	SX-DD'	SX-FF'
Arrival Time	2032.3 yr	2050.3 yr	2032.6 yr
Peak Conc.	1.346×10^5 pCi/L	5.857×10^5 pCi/L	3.132×10^5 pCi/L
Max. Initial Conc.'	3.959×10^6 pCi/L	3.463×10^7 pCi/L	7.515×10^6 pCi/L
Arrival Time	2050.7 yr	2052.7 yr	2051.3 yr
Peak Conc.	2.661×10^3 µg/L	4.453×10^4 µg/L	3.829×10^3 µg/L
Max. Initial Conc.	1.107×10^5 µg/L	1.847×10^6 µg/L	1.220×10^5 µg/L
Arrival Time	2031.9 yr	2050.3 yr	2031.3 yr
Peak Conc.	5.988×10^5 µg/L	8.148×10^6 µg/L	5.137×10^5 µg/L
Max. Initial Conc.	1.714×10^7 µg/L	3.678×10^7 µg/L	1.173×10^7 µg/L

E.4.13 NO BARRIER AND 200,000 GAL WATER-LINE LEAK CASE (CASE 13)

The no barrier and 200,000 gal water-line leak suite of simulations, Case 13, investigated solute transport through one cross-section considering natural surface infiltration and a closure barrier by the year 2040. This suite of simulations differs from the Case 1 simulations in that a water-line leak occurs for tank SX-115 in cross-section SX-FF'. The water-line leak was modeled as a point source of water (200,000 gal over a 5-day period) spread over a 15 ft radius between tanks SX-114 and SX-115. The 15 ft radius leak area was translated to the two-dimensional simulation by using a computational grid width of 1 ft and assuming that the center of the circular leak area was situated on the center line between tanks. This approach results in a two-dimensional water-line leak of 8,488 gal over a 5-day period. These simulations were initialized using a steady-flow solution defined by the surface recharge rate of 100 mm/yr and a hydraulic gradient in the unconfined aquifer. Inventories of the four contaminant species were initialized using the uniform distribution pattern. Plot-file output for these simulations was generated at the years 2000, 2000.0137, 2000.0274, 2000.0685, 2000.137, 2000.5, 2001, 2040, 2540, and 3000 and include values for the aqueous saturation, aqueous pressure, aqueous moisture content, and concentrations for the four solute species.

The flow environment following the leak event is shown in a series of color-scaled images of aqueous saturation at 5, 10, 25, 50, 183, and 365 days after the leak in Figures E.23 through E.28, respectively. After 5 days (Figure E.23), the 200,000 gal leak has completely saturated the backfill material between tanks SX-114 and SX-115, with a portion of the saturated zone extending above the tank dome and below the tank bottom. After 10 days (Figure E.24), the

leak-water has descended into the coarser grained gravelly-sand strata. At 25 and 50 days (Figures E.25 and E.26), the leak has passed through and migrated along the gravelly-sand strata, crossed the tanks SX-114 and SX-115 domes, and started to form perched water above the Plio-Pleistocene strata. Between 50 days and 1 year (Figures E.27 and E.28), the *leak* plume descended through the Plio-Pleistocene strata, reached the groundwater, and formed *two* auxiliary plumes from the *leak* water that crossed the tank domes. After one year, the saturation field had not returned to steady-flow conditions (Figure E.28). This result differs from the 25,000 gal leak, where the saturation field had returned to steady-flow conditions after 1 year.

Figure E.23. Case 13 Aqueous-Phase Saturation at 2000 plus 5 days for Cross-Section SX-FF'

**Figure E.24. Case 13 Aqueous-Phase Saturation at
2000 plus 10 days for Cross-Section SX-FF'**

**Figure E.25. Case 13 Aqueous-Phase Saturation at
2000 plus 25 days for Cross-Section SX-FF'**

Figure E.26. Case 13 Aqueous-Phase Saturation at 2000 plus 50 days for Cross-Section SX-FF'

Figure E.27. Case 13 Aqueous-Phase Saturation at 2000 plus 183 days for Cross-Section SX-FF'

Figure E.28. Case 13 Aqueous-Phase Saturation at 2000 plus 365 days for Cross-Section SX-FF'

Solute BTCs at the first compliance point for cross-section SX-FF' are shown in Attachment E3, Figures E3.187 through E3.189 for the three solute species (technetium-99, chromium, and nitrate), respectively. BTCs for cross-sections S-CC' and SX-DD' are shown in Figures E3.181 through E3.186. Aqueous fluxes at the water table for the three cross-sections are shown in Figures E3.190 through E3.192. Peak concentrations and arrival times for the BTCs at the first compliance boundary are shown in Table E.30. Area-weighted averages of the solute BTCs were generated for the three solute species and are shown in Attachment E3, Figures E3.193 through E3.195 for technetium-99, chromium, and nitrate, respectively. The saturation fields (Figures E.23 through E.28) showed saturation around the tank domes and the leak plumes rapidly descending through various strata. However, the BTCs at the WMA S-SX boundary suggest only slight differences in shapes and arrival concentrations (Attachment E3, Figures E3.187 through E3.189). Arrival times for the solutes in cross-section SX-FF' were advanced by approximately three years, but the peak concentrations were decreased, compared against the Case 1 and Case 3. Decreases in peak concentrations were a direct result of dilution due to the leak event.

Table E.30. Peak Concentrations and Arrival Times at the First Compliance Point (i.e., WMA S-SX Boundary) for Case 13

Parameter	SX-FF'
Arrival Time	2027.5 yr
Peak Conc.	2.445×10^5 pCi/L
Max. Initial Conc.'	5.074×10^6 pCi/L
Arrival Time	2049.3 yr
Peak Conc.	4.323×10^3 µg/L
Max. Initial Conc.	1.089×10^5 µg/L
NO₃	
Arrival Time	2028.5 yr
Peak Conc.	9.522×10^5 µg/L
Max. Initial Conc.	3.616×10^7 µg/L

The impact on the transport of contaminants of the 200,000 gal leak event is shown by comparing the distribution of technetium-99 at 2001 and 2040 (Figures E.29 and E.30). By 2001, the technetium-99 concentration field has been deformed toward the water table within the leak-plume column. This deformation alters the shape of the BTC (Attachment E3, Figure E3.187), but the undisturbed regions of the technetium-99 plume, outside of the leak-plume column, descend in response to the rate of meteoric recharge over a 40-year period. The similarity in technetium-99 plumes for 2040 below tanks SX-113 and SX-115 (Figure E.30) shows this effect.

Figure E.29. Case 13 Technetium-99 Aqueous Concentration at 2001 for Cross-section SX-FF'

Figure E.30. Case 13 Technetium-99 Aqueous Concentration at 2040 for Cross-Section SX-FF'

E.4.14 THREE-DIMENSIONAL SIMULATIONS

The objective of this suite of simulations is to determine the differences in results between the simulations constrained along a two-dimensional cross-section compared to the results of a simulation extended to three dimensions. Specifically, the two-dimensional cross-section simulations are along the maximum diameter of the rows of tanks, focusing the recharge over the cross-section within the most narrow zones between the tanks.

A three-dimensional simulation was constructed from a one-quarter section around tank SX-108 (Attachment E3, Figure E3.196). The geology around the tank (from east/west cross-section SX-DD' in the x and z directions) and inventory were duplicated and extended toward the north (i.e., y-direction). The radial extent of the cross-section extends to the midpoint between tanks SX-108 and SX-109 to the west and between tank SX-105 to the north. Attachment E3, Figure E3.197 shows the zonations along the southern-most y-plane, which has the maximum radius of the tank (i.e., the same plane used in the two-dimensional simulations). Transient simulations were conducted using the inventory and recharge rates from Case 1 with the three-dimensional domain and with a two-dimensional domain along the southern-most y-plane for direct comparison of results. The tank SX-108 three-dimensional simulation domain consisted of 119,422 nodes ($x, y, z = 29 \times 29 \times 142$ nodes). Within this domain, approximately 12,000 nodes were inactive, representing the tank itself. The three-dimensional simulation execution time was approximately 5 days for a 1,000-year simulation (0.333 year time step) running on a 600-Mhz Pentium II processor with 256 MB RAM.

Attachment E3, Figure E3.198 shows the steady-flow volumetric water flux vectors in the x-z directions for three y-planes (front, middle, and back) within the three-dimensional domain from the 100mm/yr recharge rate used for the first 40 years. These vectors illustrate the umbrella-effect of the tanks, where the recharge sheds from the top of the tank. The highest water fluxes occur in the thinnest zone on the front plane (i.e., $y=1$). Directly below the tank, the vectors show water moving back under the tank. Variations in the water fluxes near the tanks are dampened out towards the bottom of the domain resulting in a relatively uniform flow field in the lower half. The impact of the geology is also illustrated in Figure E3.198 where the vectors are refracted from the sloping bottom contact of Unit 3 (gravelly sandsandy gravel) at a depth of 24.4 to 30.5 m (80 to 100ft) below ground surface. Volumetric water fluxes are shown in the x-y directions at 4 different depths (2-planes) around the tanks in Figures E3.199 and E3.200. These figures show relatively high water fluxes in the x-y direction moving away from the tanks across upper dome (Figure E3.199) and moving back under the tanks below the bottom (Figure E3.200). At depths between the upper dome and bottom of the tank, water fluxes are dominantly vertical (2-direction) and very low in the x-y plane (see Figures E3.199 and E3.200).

Figure E3.201 shows the aqueous saturation along three different planes (front, middle, and back) in the y-direction at the beginning of the simulation (i.e., year 2000 with 100mm/yr recharge). The impact of the tank on aqueous saturations can still be seen on the back (northern-most) y plane, which is 3 m (10 ft) north of the edge of the tank. Figure E3.202 shows the results of the technetium-99 plume along three y-planes by year 2040 (compare to initial conditions in Figure E3.197). Figure E3.203 shows a comparison of the technetium-99 mass fluxes at the bottom of the domain for nodes on the east, center, and west of the two y-planes on

the north and south of the domain ($y=1$ and $y=29$). No variation was seen in the water fluxes for these nodes.

A comparison of the water and technetium-99 fluxes at the bottom of the simulation domain between the three-dimensional tank SX-108 and two-dimensional tank SX-108 simulations is shown in Figures E3.204 and E3.205. These figures compare the two-dimensional simulation results with the three-dimensional results from the front plane and the average over the entire three-dimensional domain. These data were scaled to unit widths. The results show little difference between the water fluxes over the 1,000-year duration of these simulations (Figure E3.204). While the simulated mass fluxes were similar overall, the peak technetium-99 mass fluxes (around year 2050) were slightly higher in the three-dimensional simulation than for the two-dimensional simulation. The peak technetium-99 mass flux for the front plane ($y=1$) of the three-dimensional simulation was also slightly higher than the mass flux average for the entire three-dimensional domain.

E.4.15 SOLUTE MASS BALANCE

Mass balance checks were performed on the non-decaying solutes (i.e., nitrate and chromium) for each combination of simulation case and cross-section, using Equation E. 18.

$$m_{error} = \frac{m_{initial} - m_{final} - m_{exiting}}{m_{initial}} \quad (E.18)$$

where:

m_{error} = mass balance error, expressed in percent

$m_{initial}$ = initial solute inventory computed from the STOMP plot-file output at the year 2000

m_{final} = final solute inventory computed from the STOMP plot-file output at the year 3000

$m_{exiting}$ = integrated solute inventory leaving the computation domain, computed from the STOMP surface-flux output.

Initial and final solute masses were computed using a two-step process: (1) STOMP plot-file outputs were converted to two-dimensional Tecplot format using the utility PlotTec; (2) solute mass was integrated using the Tecplot statistical tools package. The solute mass leaving the computational domain through the groundwater was determined using surface-flux output, defined for the western surfaces below the water table. The surface-flux output provided both the solute-flux rate and integral. Other than solving the solute mass conservation equations, the STOMP simulator contains no algorithms for correcting local or global mass. Therefore, mass balance errors, reported below represent the actual mass balance errors from the conservation equations. Mass balance errors, expressed as percent error, are shown in Table E.3 1 for the non-decaying species nitrate and chromium. The average mass balance error for the simulations without concentration dependent density and viscosity was $1.90 \times 10^{-5} \%$ and for those simulations with concentration dependent density and viscosity was $5.48 \times 10^{-2} \%$. The simulations with concentration dependent density and viscosity showed higher mass balance errors, because of the loose coupling between the aqueous-phase flow properties and the solute

concentration. This level of error in the conservation of solute mass, indicates that a fully coupled solution approach was not needed for the investigated simulations.

Table E.31. Solute Mass Balance Errors

<i>inerror</i>	Cross-Section S-CC'		Cross-Section SX-DD'		Cross-Section SX-FF'	
	Cr	NO ₃	Cr	NO ₃	Cr	NO ₃
Case 1	4.75×10^{-6}	5.52×10^{-11}	1.48×10^{-5}	3.94×10^{-11}	3.65×10^{-7}	5.69×10^{-11}
Case 2	1.33×10^{-1}	1.68×10^{-5}	2.06×10^{-7}	1.09×10^{-5}	5.33×10^{-11}	1.29×10^{-5}
Case 3	4.75×10^{-11}	5.52×10^{-6}	1.48×10^{-5}	3.94×10^{-11}	1.39×10^{-1}	5.76×10^{-11}
Case 5	3.03×10^{-5}	1.01×10^{-5}	4.03×10^{-1}	3.25×10^{-5}	5.94×10^{-5}	4.13×10^{-6}
Case 6	2.97×10^{-7}	2.18×10^{-5}	2.91×10^{-5}	4.49×10^{-1}	2.87×10^{-5}	1.12×10^{-1}
Case 7	6.65×10^{-1}	1.41×10^{-1}	4.03×10^{-1}	3.21×10^{-5}	1.32×10^{-5}	1.11×10^{-5}
Case 8	4.56×10^{-2}	2.19×10^{-2}	9.83×10^{-2}	9.04×10^{-2}	5.06×10^{-1}	2.20×10^{-1}
Case 9	2.46×10^{-7}	1.80×10^{-5}	2.07×10^{-1}	4.32×10^{-11}	4.32×10^{-5}	2.44×10^{-5}
Case 10	1.77×10^{-6}	2.23×10^{-5}	5.89×10^{-1}	3.76×10^{-11}	2.02×10^{-5}	1.42×10^{-1}
Case 11	9.80×10^{-6}	4.78×10^{-11}	1.95×10^{-4}	1.79×10^{-5}	5.23×10^{-5}	8.15×10^{-11}
Case 12	4.56×10^{-1}	1.05×10^{-5}	1.57×10^{-5}	1.05×10^{-5}	1.97×10^{-5}	3.28×10^{-11}
Case 13	4.75×10^{-6}	5.52×10^{-11}	1.48×10^{-5}	3.94×10^{-11}	1.12×10^{-11}	4.12×10^{-11}

E5.0 STREAMTUBE MODELING RESULTS

An analytical streamtube model was used to route the simulated WMA S-SX average concentrations for each case to three compliance locations: 200 West Area fence, 200 Area exclusion boundary (located approximately 1.25 km [0.78 mi] east of the 200 East Area), and the Columbia River. The analytic streamtube model was based on an approach described by Baetsle (1969), as documented in Freeze and Cherry (1979). The streamtube model assumes transport from a point source, represented by a series of solute slugs, and considers longitudinal, lateral, and transverse vertical dispersion; molecular diffusion; and first order decay. The method of superposition was used to integrate the individual slug sources.

Distances and travel times from WMA S-SX to the three compliance points were derived from steady-state VAM3D unconfined aquifer flow simulations of the Hanford Site (Lu 1996). The simulation results represent 'post-Hanford' or future conditions representing the water table at the Site without the additional impact of any unconfined aquifer discharges. Results of the VAM3D simulated hydraulic heads and streamlines are shown in Figures E.5 and E.6; these figures are based on Lu (1996). Two streamlines from Figure E.6 starting at S tank farm and SX tank farm were used to determine the unconfined aquifer path length to the three compliance points. Travel markers indicating 20-year intervals on the streamlines were used to estimate the travel time to the three Compliance points. The two streamlines (for S and SX tank farms) had similar lengths and travel times to the compliance points, resulting in only one estimate for WMA S-SX (see Table E.32). Both of these streamlines move roughly east from WMA S-SX toward the Columbia River on the south side of Gable Mountain. Other groundwater flow simulations of the Hanford Site have shown the potential for a different pathline from WMA S-SX that goes northward through the Gable Mountain/Gable Butte gap. These pathlines were not considered in this analysis.

Compliance Point	Distance (mi)	Time (yrs)
200 West fence	1.12	140
Exclusion Boundary	6.52	300
Columbia River Shoreline	14.0	500

Given the large variation in groundwater velocities between the three compliance points (see Table E.33), three streamtubes were constructed representing the aquifer between WMA S-SX and each compliance point. Solute mass **flux** across WMA S-SX boundary was a composite of the simulated aquifer outlet mass fluxes from the S-CC', SX-DD', and SX-FF' cross-sections and was converted into slugs of mass **as** input to the analytical streamtube model. Groundwater velocities for each streamtube are constant.

Table E.33. Streamtube Characteristics

From	To	(mi)	(ft/day)
WMA S-SX	200 West fence	1.12	0.116
200 West fence	Exclusion boundary	5.40	0.488
Exclusion boundary	Columbia River	7.48	OS41

A FORTRAN program was written to implement the mass flux conversion to time varying solute slugs, the analytical solution of Baetsle (1969), and superpositioning of the time-varying mass fluxes. The BTCs for each case and each species (i.e., technetium-99, chromium, and nitrate) were calculated from the streamtube from each compliance boundary, using the FORTRAN program.

The two-dimensional transport simulations (Section E.3.0) yielded solute mass **flux** and concentration at the WMA S-SX boundary along the tank centerlines for the three cross-sections (S-CC', SX-DD', and SX-FF'), as shown in Figure E.31. Translation of the centerline solute mass flux or concentration to an average value across the WMA boundary was computed using two translations. In the first translation, the centerline quantities are converted to average quantities on the WMA boundary line within the regions shown in Figure E.31 as the cross-section projections. The length of the cross-section projection equals the mean inventory diameter, where the mean inventory diameter was computed for each combination of solute specie and concentration, as described in the inventory section (Section E.2.4.3). As shown graphically in Figure E.31, the mean inventory diameter is *not* the tank diameter.

Off centerline solute mass flux and concentration are computed by assuming the concentration distribution shown in Equation E.19.

$$C_{\ell}(x) = \hat{C}_{\ell} \frac{l_c(x)}{\langle D \rangle} = \hat{C}_{\ell} \frac{\sqrt{\langle D \rangle^2 - 4x^2}}{\langle D \rangle} \quad (\text{E.19})$$

where:

$C_{\ell}(x)$ = solute mass flux or concentration as a function of distance x along the WMA boundary

$\hat{C}_{\ell}$ = tank centerline solute mass flux or concentration

$l_c(x)$ = chord length across the mean inventory circle as a function of distance x along the WMA boundary

$\langle D \rangle$ = mean inventory diameter

x = distance from the tank centerline along the WMA boundary.

Figure E.31. Translation Geometry

The average solute mass flux or concentration is computed by integrating Equation E. 19, as shown in Equation E.20.

$$\tilde{C}_\ell = \hat{C}_\ell \int_0^{\langle D \rangle/2} \frac{2\sqrt{\langle D \rangle^2 - 4x^2}}{\langle D \rangle^2} dx = \hat{C}_\ell \frac{\pi}{4} \quad (\text{E.20})$$

where:

$\tilde{C}_\ell$ = average solute mass flux or concentration along the WMA boundary within the cross-section projection.

An average solute mass flux or concentration is computed according to Equation E.20 for the three cross-sections (i.e., $\tilde{C}_\ell^{scc'}$ for S-CC', $\tilde{C}_\ell^{sxdd'}$ for SX-DD', and $\tilde{C}_\ell^{sxff'}$ for SX-FF').

The three cross-sectional average solute mass fluxes or concentrations are translated to a single average solute mass flux or concentration for the entire WMA S-SX boundary length using length-weighted averaging according to Equation E.21.

$$\bar{C}_\ell = \sum_{i=scc', sxdd', sxff'} \frac{\langle D^i \rangle}{L_{WMA}} \tilde{C}_\ell^i \quad (\text{E.21})$$

where:

$\bar{C}_\ell$ = average solute mass flux or concentration for the WMA boundary

$\langle D^i \rangle$ = mean inventory diameter for cross-section i

L_{WMA} = north-south length of the WMA S-SX boundary.

Results of the streamtube analyses are summarized in Tables E.34 through E.36, showing the peak time (year) and peak concentration for each case and compliance location, for the three species (technetium-99, chromium, and nitrate), respectively. Peak concentrations and times are a direct result of the superposition of mass fluxes from cross-sections S-CC', SX-DD, and SX-FF' averaged over the fence-line of the WMA.

Table E.34. Streamtube Analysis Summary for Technetium-99

Tc-99 Cone.	WMA S-SX		200 West fence		Exclusion Boundary		Columbia River	
(pCi/L)	Time	Cone.	Time	Conc.	(pCi/L)	Time	Conc.	Time
Case 1	2046	6.85E+04	2181	4.89E+03	2344	3.80E+02	2545	1.28E+02
Case 2	2030	2.90E+04	2179	1.91E+03	2341	1.47E+02	2543	5.11E+01
Case 3	2046	6.74E+04	2180	4.89E+03	2344	3.79E+02	2545	1.29E+02
Case 4	2046	6.83E+04	2181	4.89E+03	2344	3.79E+02	2545	1.28E+02
Case 5	2044	7.49E+04	2179	5.29E+03	2342	4.11E+02	2543	1.39E+02
Case 6	2029	3.44E+04	2178	2.09E+03	2340	1.62E+02	2542	5.61E+01
Case 7	2011	1.71E+05	2149	6.89E+03	2314	5.42E+02	2514	1.78E+02
Case 8	2046	6.92E+04	2180	4.96E+03	2344	3.85E+02	2545	1.30E+02
Case 9	2061	3.53E+04	2203	2.50E+03	2365	1.91E+02	2567	6.67E+01
Case 10	2075	1.74E+04	2223	1.32E+03	2384	9.97E+01	2586	3.54E+01
Case 11	3000*	4.34E+03	2312	3.08E+02	2471	2.26E+01	2673	8.28E+00
Case 12	2046	6.87E+04	2180	4.95E+03	2344	3.84E+02	2545	1.30E+02
Case 13	2047	6.31E+04	2179	4.76E+03	2342	3.68E+02	2543	1.25E+02

Note: Groundwater limit 900 pCi/L.

*Peak concentrations arrive after year 3000.

Table E.35. Streamtube Analysis Summary for Chromium

Cr Conc.	WMA S-SX		200 West fence		Exclusion Boundary		Columbia River	
(µg/L)	Time	Conc.	Time	Conc.	(µg/L)	Time	Conc.	Time
Case 1	2052	7.33E+03	2191	4.49E+02	2354	3.49E+01	2556	1.19E+01
Case 2	2057	1.02E+03	2210	8.55E+01	2370	6.44E+00	2573	2.31E+00
Case 3	2052	7.34E+03	2191	4.52E+02	2354	3.51E+01	2555	1.20E+01
Case 4	2052	7.30E+03	2191	4.47E+02	2354	3.48E+01	2556	1.18E+01
Case 5	2051	8.71E+03	2188	5.23E+02	2351	4.08E+01	2552	1.38E+01
Case 6	2051	1.29E+03	2205	1.03E+02	2365	7.76E+00	2568	2.77E+00
Case 7	2017	1.49E+04	2157	7.78E+02	2321	6.09E+01	2522	2.02E+01
Case 8	2052	7.42E+03	2191	4.55E+02	2354	3.54E+01	2555	1.20E+01
Case 9	2074	2.04E+03	2226	1.54E+02	2386	1.17E+01	2589	4.14E+00
Case 10	2119	6.38E+02	2272	5.55E+01	2430	4.11E+00	2632	1.50E+00
Case 11	3000*	3.86E+02	3000*	7.27E+00	2771	5.13E-01	2972	1.89E-01
Case 12	2052	7.28E+03	2191	4.51E+02	2354	3.51E+01	2555	1.19E+01
Case 13	2052	7.20E+03	2189	4.55E+02	2353	3.53E+01	2554	1.20E+01

Note: Groundwater limit 50 µg/L.

*Peak concentrations arrive after year 3000.

Table E.36. Streamtube Analysis Summary for Nitrate

NO₃ Cone.	WMA S-SX		200 West fence		Exclusion Boundary		Columbia River	
(µg/L)	Time	Cone.	Time	Cone.	Time	Cone.	Time	Cone.
Case 1	2041	1.28E+05	2178	9.49E+03	2342	7.37E+02	2542	2.49E+02
Case 2	2029	6.88E+04	2177	4.31E+03	2339	3.34E+02	2541	1.15E+02
Case 3	2041	1.27E+05	2178	9.50E+03	2341	7.38E+02	2542	2.50E+02
Case 4	2041	1.28E+05	2178	9.46E+03	2342	7.35E+02	2542	2.49E+02
Case 5	2038	1.39E+05	2176	1.02E+04	2340	7.96E+02	2540	2.69E+02
Case 6	2027	8.41E+04	2175	4.81E+03	2337	3.73E+02	2539	1.29E+02
Case 7	2007	3.57E+05	2148	1.31E+04	2312	1.03E+03	2513	3.39E+02
Case 8	2041	1.29E+05	2178	9.61E+03	2341	7.47E+02	2542	2.52E+02
Case 9	2058	7.76E+04	2199	5.32E+03	2361	4.09E+02	2563	1.42E+02
Case 10	2074	4.12E+04	2221	3.04E+03	2382	2.31E+02	2584	8.17E+01
Case 11	2167	8.45E+03	2315	7.45E+02	2473	5.48E+01	2676	2.01E+01
Case 12	2039	1.28E+05	2177	9.63E+03	2340	7.48E+02	2541	2.53E+02
Case 13	2041	1.21E+05	2177	9.42E+03	2340	7.30E+02	2541	2.48E+02

Note: Groundwater limit = 15,000 µg/l
 *Peak concentrations are after year 2000.

The first streamtube extended from the WMA boundary to the 200 West fence compliance boundary; peak concentrations at the 200 West fence generally decreased to less than 10% of the WMA boundary concentration. Those simulations with broader BTCs at the WMA boundary had lower percent decreases; whereas, those with sharper BTCs had greater percent decreases from longitudinal dispersion. The second streamtube extended from the 200 West fence to the 200 Area exclusion boundary. Again, the concentrations at the 200 Area exclusion boundary generally decreased to less than 10% of the 200 West fence boundary concentration. Results for the final streamtube (between the 200 Area exclusion boundary and Columbia River) showed the smallest decrease in peak concentrations for all the streamtubes, even though the residence time in this streamtube was the longest. The peak concentrations at the Columbia River boundary generally decreased to less than 40% of the 200 Area exclusion boundary concentration. The reason for the lower percentage decrease in concentrations for this streamtube is that the peak concentrations have already been significantly attenuated by the earlier two streamtubes resulting in larger and broader pulses. The increase in unconfined aquifer velocity accounted for most of the decrease in peak concentrations for this streamtube.

E.6.0 HUMAN HEALTH RISK AND DOSE RESULTS

This section presents the results of the human health risk and dose assessment. The risk and dose values presented are based on the groundwater concentrations generated through contaminant transport modeling (Sections E.1.0 and E.2.0) and were calculated using the approach described in Section E.3.0. Groundwater concentration values from cross-sections S-CC', SX-DD', and SX-FF' at the WMA S-SX boundary used Equation E.19 in Section E.5.0 to calculate the risk and dose values with the methodology described in Section E.3.0. Note that risk and dose results are presented only for a select group of simulation cases (Table E.37). Results for these cases are representative of the larger set of cases considered in the contaminant transport analysis and include information on the impacts associated with existing conditions (Case 1); interim barrier use (Case 2); and variable meteoric recharge rates (Cases 9, 10, 11). The remaining cases generally represent variations around the existing conditions or interim barrier cases and are not specifically discussed in this section because their impacts are of similar magnitude to either Case 1 or 2.

Case	Description	Rationale
I	Base case (no action alternative)	Reference case. Estimation of impacts from past contaminant releases at WMA S-SX if no interim measures or interim corrective measures were implemented.
2	Barrier alternative and no water-line leaks	Interim corrective measure case. Estimation of degree to which implementation of an interim surface barrier would decrease impacts from past contaminant releases at WMA S-SX .
9	Base case with 50 m d y r meteoric recharge	Meteoric recharge sensitivity cases. Estimation of degree to which meteoric recharge modeling assumptions affect estimated base case impacts from past contaminant releases at WMA S-SX .
10	Base case with 30 mm/yr meteoric recharge	
11	Base case with 10 mm/yr meteoric recharge	

Risk and dose results for the five cases shown in Table E.37 are presented individually in Sections E.6.1 to E.6.5. As discussed in Section E.3.1, multiple exposure scenarios are considered in this assessment to account for the uncertainty of long-term Hanford Site land use. To simplify the presentation, the individual case discussions focus on the results for the industrial worker scenario. Results for all the receptor scenarios are provided in table format for each case; however, for comparison purposes, a single scenario is sufficient because the relationship between the receptor scenarios remains relatively consistent within each case. For example, regardless of the case or compliance point, the peak residential farmer ILCR is always approximately 35 times higher than the peak industrial worker ILCR, and the **MTCA** Method B peak hazard index is always approximately 2.2 times higher than the **MTCA** Method C peak hazard index.

E.6.1 BASE CASE, NO ACTION ALTERNATIVE (CASE 1)

Results for the base case (Case 1) are summarized in Table E.38. Results for Case 1 reveal three general trends that are also evident in the results for the other cases considered (Cases 2, 9, 10, 11). First, peak values for the cross-sections at the WMA S-SX boundary exceed the peak values for the downgradient compliance points. Second, peak values at the WMA S-SX boundary are highest for cross-sections SX-DD' or SX-FF', followed by cross-section S-CC'. Third, peak values at the last compliance point (i.e., the Columbia River shoreline) are generally three to four orders of magnitude lower than the peak values at the WMA S-SX boundary.

Peak values for Case 1 are the highest of the five cases considered. Between the WMA S-SX boundary and the Columbia River shoreline compliance location, the peak industrial worker ILCR varies from 9.98×10^{-3} to 1.33×10^{-6} . Peak ILCR values are driven by technetium-99. The peak industrial worker hazard index varies from 3.00×10^2 to 4.22×10^2 . Peak hazard index values are driven by chromium. The peak dose varies from 5.94×10^1 mredyr to 7.94×10^2 mredyr. Peak dose values are driven by technetium-99.

Temporal variations in ILCR for Case 1 are shown in Figure E.32 for compliance points at the WMA S-SX boundary and in Figure E.33 for compliance points between the WMA S-SX boundary and the Columbia River. Temporal variations in hazard index and dose for Case 1 are similar to those shown for ILCR. At the WMA S-SX boundary, peaks for the three cross-sections arrive within approximately the first 50 years and are all relatively sharp. Peaks at the 200 West fence, 200 Area exclusion boundary, and Columbia River shoreline compliance locations arrive after approximately 180, 350, and 550 years, respectively, and are broader than the peaks at the WMA S-SX boundary.

Figure E.32. Case 1 Industrial Worker ILCR Versus Time at WMA S-SX Boundary **Figure E.33. Case 1 Industrial Worker ILCR Versus Time at Compliance Points Between the WMA S-SX Boundary and the Columbia River**

Table E.38. Peak Long-Term Human Health Impacts for Case 1

Compliance Point	Residential Farmer		Industrial Worker		Recreational Shoreline User ^a		MTCA Method B ^b		MTCA Method C ^b		Dose to Worker
	ILCR	HI	ILCR	HI	ILCR	HI	ILCR	HI	ILCR	HI	mrem/yr
S-SX WMA Boundary	S - CC'	4.13E-02	5.07E+03	1.15E-03	1.16E+01	N/A	N/A	2.13E+02	N/A	9.75E+01	6.91E+01
	SX - DD'	3.57E-01	2.09E+04	9.98E-03	3.00E+02	N/A	N/A	2.77E+03	N/A	1.26E+03	5.94E+02
	SX - FF'	8.39E-02	6.09E+03	2.34E-03	1.96E+01	N/A	N/A	5.20E+02	N/A	2.38E+02	1.40E+02
200 West Fence	1.82E-03	7.70E+01	5.07E-05	1.60E+00	N/A	N/A	N/A	1.32E+01	N/A	6.02E+00	3.02E+00
200 Area Exclusion Boundary	1.41E-04	5.98E+00	3.94E-06	1.24E-01	N/A	N/A	N/A	1.02E+00	N/A	4.67E-01	2.35E-01
Columbia River Shoreline	4.77E-05	2.02E+00	1.33E-06	4.22E-02	2.21E-07	4.52E-03	N/A	3.48E-01	N/A	1.59E-01	7.94E-02

^aExposures defined to occur only within 400 m (1,300 ft) of the Columbia River shoreline.

^bCancer risks not shown because MTCA addresses only nonradioactive contaminants and no nonradioactive carcinogenic chemicals were identified as contaminants of concern for WMA S-SX.

HI = hazard index.

ILCR = incremental lifetime cancer risk.

MTCA = Model Toxics Control Act.

N/A = not applicable.

E.6.2 BARRIER ALTERNATIVE AND NO WATER-LINE LEAKS CASE (CASE 2)

Results for Case 2, barrier alternative and no water-line leaks, are summarized in Table E.39. Results for Case 2 show the same general trends regarding the compliance points as discussed above for Case 1. Peak values for Case 2 are generally a factor of 2 to 10 lower than the corresponding values for Case 1. Between the WMA S-SX boundary and the Columbia River shoreline, the peak industrial worker ILCR varies from 1.65×10^{-3} to 5.30×10^{-7} . Peak ILCR values are driven by technetium-99. The peak industrial worker hazard index varies from 2.99×10^1 to 8.79×10^{-3} . Peak hazard index values are driven by chromium and nitrate. The peak dose ranges from 9.85×10^1 mredyr to 3.16×10^{-2} mredyr. Peak dose values are driven by technetium-99.

Temporal variations in ILCR for Case 2 are shown in Figure E.34 for compliance points at the WMA S-SX boundary and in Figure E.35 for compliance points between the WMA S-SX boundary and the Columbia River. Temporal variations in hazard index and dose for Case 2 are similar to those shown for ILCR. At the WMA S-SX boundary, peak arrival times for the three cross-sections are similar to Case 1 but the peaks are broader in shape. All three peaks arrive within approximately the first 60 years. Peaks at the 200 West fence, 200 Area exclusion boundary, and Columbia River shoreline compliance locations are also similar to and slightly broader than Case 1 and arrive after approximately 180,350, and 550 years, respectively.

Figure E.34. Case 2 Industrial Worker ILCR Versus Time at WMA S-SX Boundary

Figure E.35. Case 2 Industrial Worker ILCR Versus Time at Compliance Points Between the WMA S-SX Boundary and the Columbia River

Table E-39. Peak Long-Term Human Health Impacts for Case 2

Compliance Point	Residential Farmer		Industrial Worker		Recreational Shoreline User ^a		MTCA Method B ^b		MTCA Method C ^b		Dose to Worker
	ILCR	HI	ILCR	HI	ILCR	HI	ILCR	HI	ILCR	HI	mrem/yr
S-SX WMA Boundary	S - CC'	2.76E-02	3.43E+03	7.68E-04	5.35E+00	N/A	N/A	1.36E+02	N/A	6.20E+01	4.61E+01
	SX - DD'	5.32E-02	3.35E+03	1.49E-03	2.99E+01	N/A	N/A	3.28E+02	N/A	1.57E+02	8.86E+01
	SX - FF'	5.91E-02	4.11E+03	1.65E-03	9.77E+00	N/A	N/A	3.39E+02	N/A	1.55E+02	9.85E+01
200 West Fence	7.08E-04	3.36E+01	1.98E-05	3.25E-01	N/A	N/A	N/A	3.38E+00	N/A	1.55E+00	1.18E+00
200 Area Exclusion Boundary	5.46E-05	2.60E+00	1.53E-06	2.45E-02	N/A	N/A	N/A	2.58E-01	N/A	1.18E-01	9.10E-02
Columbia River Shoreline	1.90E-05	9.00E-01	5.30E-07	8.79E-03	8.81E-08	9.60E-04	N/A	9.14E-02	N/A	4.18E-02	3.16E-02

^aExposures defined to occur only within 400 m (1,300 ft) of the Columbia River shoreline.^bCancer risks not shown because MTCA addresses only nonradioactive contaminants and no nonradioactive carcinogenic chemicals were identified as contaminants of concern for WMA S-SX.

HI = hazard index.

ILCR = incremental lifetime cancer risk.

MTCA = Model Toxics Control Act.

N/A = not applicable.

E.6.3 BASE CASE WITH 50 MM/YR METEORIC RECHARGE (CASE 9)

Results for Case 9, base case with 50 m d y r meteoric recharge, are summarized in Table E.40. Results for Case 9 show the same general trends regarding the compliance points as discussed above for Case 1. Peak values for Case 9 are generally a factor of 2 to 4 lower than the corresponding values for Case 1. Between the WMA S-SX boundary and the Columbia River shoreline, the peak industrial worker ILCR varies from 3.03×10^{-3} to 6.92×10^{-7} . Peak ILCR values are driven by technetium-99. The peak industrial worker hazard index varies from 6.73×10^{-1} to 1.52×10^{-2} . Peak hazard index values are driven by chromium and nitrate. The peak dose varies from 1.80×10^2 mred/yr to 4.13×10^{-2} mrem/yr. Peak dose values are driven by technetium-99.

Temporal variations in ILCR for Case 9 are shown in Figure E.36 for compliance points at the WMA S-SX boundary and in Figure E.37 for compliance points between the WMA S-SX boundary and the Columbia River. Temporal variations in hazard index and dose for Case 9 are similar to those shown for ILCR. Overall, the temporal variations for Case 9 resemble those for Case 2. At the WMA S-SX boundary, peaks for the three cross-sections have slightly delayed arrival times and broader shapes compared to Case 1. All three peaks arrive within the first 75 years. Peaks at the 200 West fence, 200 Area exclusion boundary, and Columbia River shoreline compliance locations are also slightly delayed and broadened compared to Case 1.

Figure E.36. Case 9 Industrial Worker ILCR Versus Time at WMA S-SX Boundary

Figure E.37. Case 9 Industrial Worker ILCR Versus Time at Compliance Points Between the WMA S-SX Boundary and the Columbia River

Table E.40. Peak Long-Term Human Health Impacts for Case 9

Compliance Point	Residential Farmer		Industrial Worker		Recreational Shoreline User ^a		MTCA Method B ^b		MTCA Method C ^b		Dose to Worker
	ILCR	HI	ILCR	HI	ILCR	HI	ILCR	HI	ILCR	HI	mrem/yr
S-SX WMA Boundary	S - CC'	2.76E-02	3.40E+03	7.70E-04	6.29E+00	N/A	N/A	1.40E+02	N/A	6.39E+01	4.63E+01
	SX - DD'	1.08E-01	6.45E+03	3.03E-03	6.73E+01	N/A	N/A	6.95E+02	N/A	3.18E+02	1.80E+02
	SX - FF'	5.81E-02	4.23E+03	1.62E-03	1.19E+01	N/A	N/A	3.58E+02	N/A	1.64E+02	9.69E+01
200 West Fence		9.27E-04	4.20E+01	2.59E-05	5.63E-01	N/A	N/A	5.21E+00	N/A	2.38E+00	1.54E+00
200 Area Exclusion Boundary		7.10E-05	3.22E+00	1.99E-06	4.29E-02	N/A	N/A	3.97E-01	N/A	1.81E-01	1.18E-01
Columbia River Shoreline		2.48E-05	1.12E+00	6.92E-07	1.52E-02	1.15E-07	1.64E-03	1.40E-01	N/A	6.40E-02	4.13E-02

^aExposures defined to occur only within 400 m (1,300 ft) of the Columbia River shoreline.^bCancer risks not shown because MTCA addresses only nonradioactive contaminants and no nonradioactive carcinogenic chemicals were identified as contaminants of concern for WMA S-SX.

HI = hazard index.

ILCR = incremental lifetime cancer risk.

MTCA = Model Toxics Control Act.

N/A = not applicable.

E.6.4 BASE CASE WITH 30 MM/YR METEORIC RECHARGE (CASE 10)

Results for Case 10, base case with 30 mm/yr meteoric recharge, are summarized in Table E.41. Results for Case 10 show the same general trends regarding the compliance points as discussed above for Case 1. Peak values for Case 10 are generally a factor of 2 to 15 lower than the corresponding values for Case 1. Between the WMA S-SX boundary and the Columbia River shoreline, the peak industrial worker ILCR varies from 1.01×10^{-3} to 3.67×10^{-3} . Peak ILCR values are driven by technetium-99. The peak industrial worker hazard index varies from 2.07×10^{-3} to 5.69×10^{-3} . Peak hazard index values are driven by chromium and nitrate. The peak dose ranges from 6.01×10^{-3} mrem/yr to 2.19×10^{-2} mrem/yr. Peak dose values are driven by technetium-99.

Temporal variations in ILCR for Case 10 are shown in Figure E.38 for compliance points at the WMA S-SX boundary and in Figure E.39 for compliance points between the WMA S-SX boundary and the Columbia River. Temporal variations in hazard index and dose for Case 10 are similar to those shown for ILCR. At the WMA S-SX boundary, peaks for the three cross-sections are further delayed in arrival times and have even broader shapes compared to Case 9. The three peaks arrive within approximately 125 years. The curves for the three cross-sections begin to rise again after approximately 900 years and are still rising at the end of the 1,000-year analysis period. Peaks at the 200 West fence, 200 Area exclusion boundary, and Columbia River shoreline compliance locations are also further delayed and broadened compared to Case 9.

Figure E.38. Case 10 Industrial Worker ILCR Versus Time at WMA S-SX Boundary

Figure E.39. Case 10 Industrial Worker ILCR Versus Time at Compliance Points Between the WMA S-SX Boundary and the Columbia River

Table 41. Peak Health Impacts for Case 10

Compliance Point	Residential Farmer		Industrial Worker		Recreational Shoreline User ^a		MTCA Method B ^b		MTCA Method C ^b		Dose to Worker
	ILCR	HI	ILCR	HI	ILCR	HI	ILCR	HI	ILCR	HI	
S-SX WMA Boundary	S - CC'	1.56E-02	1.95E+03	4.36E-04	3.08E+00	N/A	N/A	7.75E+01	N/A	3.54E+01	2.61E+01
	SX - DD'	3.23E-02	1.98E+03	9.02E-04	2.07E+01	N/A	N/A	1.98E+02	N/A	9.03E+01	5.37E+01
	SX - FF'	3.61E-02	2.60E+03	1.01E-03	6.30E+00	N/A	N/A	2.15E+02	N/A	9.82E+01	6.01E+01
200 West Fence	4.88E-04	2.36E+01	1.36E-05	2.11E-01	N/A	N/A	N/A	2.23E+00	N/A	1.02E+00	8.14E-01
200 Area Exclusion Boundary	3.70E-05	1.79E+00	1.03E-06	1.57E-02	N/A	N/A	N/A	1.67E-01	N/A	7.63E-02	6.17E-02
Columbia River Shoreline	1.31E-05	6.34E-01	3.67E-07	5.69E-03	6.10E-08	6.22E-04	N/A	6.02E-02	N/A	2.75E-02	2.19E-02

^aExposures assumed to occur only within 400 m (1,300 ft) of the Columbia River shoreline.

^bCancer risks not shown because MTCA addresses only nonradioactive contaminants and no contaminants of concern for WMA S-SX.

HI = hazard index.

ILCR = incremental lifetime cancer risk.

MTCA - Model Toxics Control Act.

N/A = not applicable.

E.6.5 BASE CASE WITH 10 MM/YR METEORIC RECHARGE (CASE 11)

Results for Case 11, base case with 10mm/yr meteoric recharge, are summarized in Table E.42. Results for Case 11 show the same general trends regarding the compliance points as discussed above for Case 1. Peak values for Case 11 are generally a factor of 15 to 50 lower than the corresponding values for Case 1. Between the WMA S-SX boundary and the Columbia River shoreline, the peak industrial worker ILCR varies from 5.94×10^{-4} to 8.59×10^{-8} . Peak ILCR values are driven by technetium-99. The peak industrial worker hazard index varies from 1.25×10^1 to 7.54×10^{-4} . Peak hazard index values are driven by chromium. The peak dose varies from 3.26×10^1 mredyr to 5.12×10^{-3} mredyr. Peak dose values are driven by technetium-99.

Temporal variations in ILCR for Case 11 are shown in Figure E.40 for compliance points at the WMA S-SX boundary and in Figure E.41 for compliance points between the WMA S-SX boundary and the Columbia River. Temporal variations in hazard index and dose for Case 11 are similar to those shown for ILCR. At the WMA S-SX boundary, peaks for the three cross-sections are even further delayed in arrival times and have even broader shapes compared to Case 10. The secondary elevation in ILCR values observed for Case 10 at the end of the 1,000-year analysis period is also observed for Case 11 but is more pronounced. For cross-section SX-DD', the late ILCR peak actually exceeds the earlier peak. Peaks at the 200 West Fence, 200 Area exclusion boundary, and Columbia River shoreline compliance locations are also even further delayed and broadened compared to Case 10 and arrive after approximately 300, 480, and 680 years, respectively.

Figure E.40. Case 11 Industrial Worker ILCR Versus Time at WMA S-SX Boundary

Figure E.41. Case 11 Industrial Worker ILCR Versus Time at Compliance Points Between the WMA S-SX Boundary and the Columbia River

Table E.42. Peak Long-Term Human Health Impacts for Case 11

Compliance Point	Residential Farmer		Industrial Worker		Recreational Shoreline User ^a		MTCA Method B ^b		MTCA Method C ^b		Dose to Worker
	ILCR	HI	ILCR	HI	ILCR	HI	ILCR	HI	ILCR	HI	mrem/yr
S-SX WMA Boundary	S - CC'	3.16E-03	4.08E+02	8.82E-05	7.67E-01	N/A	N/A	1.59E+01	N/A	7.25E+00	5.29E+00
	SX - DD'	1.96E-02	1.12E+03	5.49E-04	1.25E+01	N/A	N/A	1.27E+02	N/A	5.82E+01	3.26E+01
	SX - FF'	8.14E-03	5.94E+02	2.27E-04	1.43E+00	N/A	N/A	4.84E+01	N/A	2.21E+01	1.36E+01
200 West Fence	1.14E-04	5.70E+00	3.19E-06	2.81E-02	N/A	N/A	N/A	3.85E-01	N/A	1.76E-01	1.90E-01
200 Area Exclusion Boundary	8.40E-06	4.19E-01	2.35E-07	2.04E-03	N/A	N/A	N/A	2.81E-02	N/A	1.28E-02	1.40E-02
Columbia River Shoreline	3.07E-06	1.54E-01	8.59E-08	7.54E-04	1.43E-08	8.38E-05	N/A	1.03E-02	N/A	4.73E-03	5.12E-03

^aExposures defined to occur only within 400 m (1,300 ft) of the Columbia River shoreline.

^bCancer risks not shown because MTCA addresses only nonradioactive contaminants and no nonradioactive carcinogenic chemicals were identified as contaminants of concern for WMA S-SX.

HI = hazard index.

ILCR = incremental lifetime cancer risk.

MTCA = Model Toxics Control Act.

N/A = not applicable.

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ATTACHMENT E1
VADOSE ZONE INVENTORY ESTIMATES

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TABLES

E1.1.	Vadose Zone Inventory Estimates for Cs-137 for Individual Tanks	E1-1
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Table E1.1. Vadose Zone Inventory Estimates for Cs-137 for Individual Tanks

SX-107			SX-108			sx-109		
Depth (ft) bgs	1/1/00 Cs-137(Ci)	1/1/00 Cs-137 (pCi/g)	Depth (ft) bgs	1/1/00 Cs-137(Ci)	1/1/00 Cs-137 (pCi/g)	Depth (ft) bgs	1/1/00 Cs-137(Ci)	1/1/00 Cs-137 (pCi/g)
47.6-57.4	2.13E-02	3.38E+02	47.6-57.4	1.54E-01	1.76E+03	47.6-57.4	5.25E-04	2.92E+02
57.4-67.2	1.36E+04	2.63E+07	57.4-67.2	2.32E+04	1.65E+07	57.4-67.2	3.39E+02	4.65E+05
67.2-77.1	1.24E+03	3.31E+06	67.2-77.1	1.29E+04	1.34E+07	67.2-77.1	1.03E+03	6.27E+05
77.1-86.9	1.54E-01	1.60E+03	77.1-86.9	7.36E+01	2.53E+05	77.1-86.9	9.32E+02	1.14E+06
			86.9-96.8	9.81E-01	8.42E+03	86.9-96.8	2.06E+02	5.97E+05
			96.8-106.6	1.91E-01	1.26E+03	96.8-106.6	1.75E+01	2.61E+04
			106.6-116.4	9.05E-02	8.78E+02	106.6-116.4	4.15E+00	1.11E+04
			116.4-126.3	3.53E-02	2.88E+02	116.4-126.3	1.01E+00	2.13E+03
			126.3-136.1	6.28E-03	1.94E+02	126.3-136.1	2.73E-01	1.34E+03
SX-113			SX-115			S-104		
Depth (ft) bgs	1/1/00 Cs-137(Ci)	1/1/00 Cs-137 (pCi/g)	Depth (ft) bgs	1/1/00 Cs-137(Ci)	1/1/00 Cs-137 (pCi/g)	Depth (ft) bgs	1/1/00 Cs-137(Ci)	1/1/00 Cs-137 (pCi/g)
56-64	6.38E+03	1.40E+07	56-64	1.63E+04	1.07E+07	40-52	9.91E+03	1.36E+07

Table E1.2. Vadose Zone Inventory Estimates for Tc-99 for Individual Tanks (3 Sheets)

SX-107			sx-108			SX-109		
Depth (ft) bgs	Tc-99 (pCi/g soil)	Tc-99 (Ci)	Depth (ft) bgs	Tc-99 (pCi/g soil)	Tc-99 (Ci)	Depth (ft) bgs	Tc-99 (pCi/g soil)	Tc-99 (Ci)
25-26	1.53E-01	2.07E-05	25-26	1.53E-01	4.98E-05	25-26	1.53E-01	3.22E-06
44-45	9.63E-01	1.30E-04	44-45	9.63E-01	3.13E-04			
56-57	5.06E-01	6.84E-05	56-57	5.06E-01	1.65E-04	56-57	5.06E-01	1.07E-05
61-62	6.97E-01	9.43E-05	61-62	6.97E-01	2.27E-04	61-62	6.97E-01	1.47E-05
						65-66	5.32E+00	1.12E-04
55-56	5.52E+00	4.6E-04	69-70	5.52E+00	1.80E-03	69-70	5.52E+00	1.16E-04
74-75	7.72E+00	1.04E-03	74-75	7.72E+00	2.51E-03	74-75	7.72E+00	1.63E-04
79-80	1.82E+01	2.46E-03	79-80	1.82E+01	5.92E-03	79-80	1.82E+01	3.84E-04
82-83	3.93E+02	5.31E-02	82-83	3.93E+02	1.28E-01	82-83	3.93E+02	8.28E-03
90	2.75E+03	3.72E-01	90	2.75E+03	8.95E-01		2.75E+03	5.80E-02
95-96	7.08E+03	9.57E-01	95-96	7.08E+03	2.30E+00	95-96	7.08E+03	1.49E-01
102-103	6.14E+03	8.30E-01	102-103	6.14E+03	2.00E+00	102-103	6.14E+03	1.29E-01
108-109	1.19E+04	1.61E+00	108-109	1.19E+04	3.87E+00	108-109	1.19E+04	2.51E-01
112	8.56E+03	1.16E+00	112	8.56E+03	2.78E+00			
127.4	3.34E+02	4.52E-02	127.4	3.34E+02	1.09E-01	127.4	3.34E+02	7.04E-03
SX-113			SX-115			S-104		
Depth (ft) bgs	Tc-99 (pCi/g soil)	Tc-99 (Ci)	Depth (ft) bgs	Tc-99 (pCi/g soil)	Tc-99 (Ci)	Depth (ft) bgs	Tc-99 (pCi/g soil)	Tc-99 (Ci)
33	0.85	4.18E-04	33	0.85	9.23E-04	33	0.85	6.47E-04
56.25	0.85	4.18E-04	56.25	0.85	9.22E-04	56.25	0.85	6.47E-04
57.5	0.85	4.18E-04	57.5	0.85	9.23E-04	57.5	0.85	6.47E-04
61.25	0.85	4.16E-04	61.25	0.85	9.19E-04	61.25	0.85	6.45E-04
62.75	0.85	4.17E-04	62.75	0.85	9.22E-04	62.75	0.85	6.46E-04
63.25	0.84	4.16E-04	63.25	0.84	9.19E-04	63.25	0.84	6.44E-04
64.75	0.84	4.16E-04	64.75	0.84	9.18E-04	64.75	0.84	6.44E-04
68	0.85	4.17E-04	68	0.85	9.20E-04	68	0.85	6.45E-04
70	0.85	4.18E-04	70	0.85	9.23E-04	70	0.85	6.47E-04
71	0.85	4.18E-04	71	0.85	9.23E-04	71	0.85	6.47E-04
73.25	12.89	6.35E-03	73.25	12.89	1.40E-02	73.25	12.89	9.84E-03
73.75	41.75	2.06E-02	73.75	41.75	4.54E-02	73.75	41.75	3.19E-02
74.25	47.07	2.32E-02	74.25	47.07	5.12E-02	74.25	47.07	3.59E-02
75.25	33.07	1.63E-02	75.25	33.07	3.60E-02	75.25	33.07	2.52E-02
79.25	29.44	1.45E-02	79.25	29.44	3.20E-02	79.25	29.44	2.25E-02
79.75	25.43	1.25E-02	79.75	25.43	2.77E-02	79.75	25.43	1.94E-02

Table E1.2. Vadose Zone Inventory Estimates for Tc-99 for Individual Tanks (3 Sheets)

SX-113			SX-115			S-104		
Depth (ft) bgs	Tc-99 (pCi/g soil)	Tc-99 (Ci)	Depth (ft) bgs	Tc-99 (pCi/g soil)	Tc-99 (Ci)	Depth (ft) bgs	Tc-99 (pCi/g soil)	Tc-99 (Ci)
80.25	32.11	1.58E-02	80.25	32.11	3.49E-02	80.25	32.11	2.45E-02
87	7.19	3.54E-03	87	7.19	7.83E-03	87	7.19	5.49E-03
88.4	47.61	2.35E-02	88.4	47.61	5.18E-02	88.4	47.61	3.63E-02
95	30.57	1.51E-02	95	30.57	3.33E-02	95	30.57	2.33E-02
99	7.97	3.93E-03	99	7.97	8.67E-03	99	7.97	6.08E-03
100	34.63	1.71E-02	100	34.63	3.77E-02	100	34.63	2.64E-02
103.25	12.89	6.35E-03	103.25	12.89	1.40E-02	103.25	12.89	9.83E-03
105.25	12.73	6.28E-03	105.25	12.73	1.39E-02	105.25	12.73	9.71E-03
107	36.31	1.79E-02	107	36.31	3.95E-02	107	36.31	2.77E-02
116	36.93	1.82E-02	116	36.93	4.02E-02	116	36.93	2.82E-02
123.8	82.59	4.07E-02	123.8	82.59	8.99E-02	123.8	82.59	6.30E-02
124.35	82.59	4.07E-02	124.35	82.59	8.99E-02	124.35	82.59	6.30E-02
125.35	222.01	1.09E-01	125.35	222.01	2.42E-01	125.35	222.01	1.69E-01
126.35	362.77	1.79E-01	126.35	362.77	3.95E-01	126.35	362.77	2.77E-01
129.45	542.80	2.68E-01	129.45	542.80	5.91E-01	129.45	542.80	4.14E-01
132.45	390.39	1.92E-01	132.45	390.39	4.25E-01	132.45	390.39	2.98E-01
134.45	99.60	4.91E-02	134.45	99.60	1.08E-01	134.45	99.60	7.60E-02
136	364.64	1.80E-01	136	364.64	3.97E-01	136	364.64	2.78E-01
138.2	346.77	1.71E-01	138.2	346.77	3.77E-01	138.2	346.77	2.65E-01
140.65	328.05	1.62E-01	140.65	328.05	3.57E-01	140.65	328.05	2.50E-01
141.65	252.62	1.24E-01	141.65	252.62	2.75E-01	141.65	252.62	1.93E-01
142.75	281.68	1.39E-01	142.75	281.68	3.07E-01	142.75	281.68	2.15E-01
144.2	216.55	1.07E-01	144.2	216.55	2.36E-01	144.2	216.55	1.65E-01
145.65	185.12	9.12E-02	145.65	185.12	2.01E-01	145.65	185.12	1.41E-01
146.65	286.49	1.41E-01	146.65	286.49	3.12E-01	146.65	286.49	2.19E-01
147.55	48.46	2.39E-02	147.55	48.46	5.27E-02	147.55	48.46	3.70E-02
148.55	190.95	9.41E-02	148.55	190.95	2.08E-01	148.55	190.95	1.46E-01
149.55	186.28	9.18E-02	149.55	186.28	2.03E-01	149.55	186.28	1.42E-01
152.2	56.32	2.78E-02	152.2	56.32	6.13E-02	152.2	56.32	4.30E-02
153.15	20.78	1.02E-02	153.15	20.78	2.26E-02	153.15	20.78	1.59E-02
155.15	3.42	1.68E-03	155.15	3.42	3.72E-03	155.15	3.42	2.61E-03
156.1	30.93	1.52E-02	156.1	30.93	3.37E-02	156.1	30.93	2.36E-02
156.55	10.58	5.22E-03	156.55	10.58	1.15E-02	156.55	10.58	8.07E-03
157.75	1.14	5.60E-04	157.75	1.14	1.24E-03	157.75	1.14	8.67E-04
158.65	2.68	1.32E-03	158.65	2.68	2.92E-03	158.65	2.68	2.05E-03

Table E1.2. Vadose Zone Inventory Estimates for Tc-99 for Individual Tanks (3 Sheets)

SX-113			SX-115			S-104		
Depth (ft) bgs	Tc-99 (pCi/g soil)	Tc-99 (Ci)	Depth (ft) bgs	Tc-99 (pCi/g soil)	Tc-99 (Ci)	Depth (ft) bgs	Tc-99 (pCi/g soil)	Tc-99 (Ci)
159.75	2.58	1.27E-03	159.75	2.58	2.81E-03	159.75	2.58	1.97E-03
161	1.63	8.03E-04	161	1.63	1.77E-03	161	1.63	1.24E-03
162	2.74	1.35E-03	162	2.74	2.98E-03	162	2.74	2.09E-03
166	1.59	7.82E-04	166	1.59	1.73E-03	166	1.59	1.21E-03
167	0.92	4.52E-04	167	0.92	9.97E-04	167	0.92	6.99E-04
175	0.56	2.76E-04	175	0.56	6.09E-04	175	0.56	4.27E-04
185	0.27	1.34E-04	185	0.27	2.97E-04	185	0.27	2.08E-04
184.8	0.40	1.99E-04	184.8	0.40	4.39E-04	184.8	0.40	3.08E-04
186	0.19	9.20E-05	186	0.19	2.03E-04	186	0.19	1.42E-04
190	0.29	1.42E-04	190	0.29	3.13E-04	190	0.29	2.20E-04
194.55	0.33	1.60E-04	194.55	0.33	3.54E-04	194.55	0.33	2.48E-04
204.45	3.14	1.55E-03	204.45	3.14	3.42E-03	204.45	3.14	2.40E-03
205.1	4.26	2.10E-03	205.1	4.26	4.64E-03	205.1	4.26	3.25E-03

Table E1.3. Vadose Zone Inventory Estimates for NO₃ for Individual Tanks (3 Sheets)

SX-107			SX-108			SX-109		
Depth (ft) bgs	NO3 (ug/g soil)	NO3 (Kg)	Depth (ft) bgs	NO3 (ug/g soil)	NO3 (Kg)	Depth (ft) bgs	NO3 (ug/g soil)	NO3 (Kg)
25-26	1.30E+01	5.23E-01	25-26	1.30E+01	1.25E+00	25-26	1.30E+01	8.13E-02
44-45	1.30E+01	5.23E-01	44-45	1.30E+01	1.25E+00	44-45	1.30E+01	8.13E-02
56-57	1.30E+01	5.23E-01	56-57	1.30E+01	1.25E+00	56-57	1.30E+01	8.13E-02
61-62	1.30E+01	5.23E-01	61-62	1.30E+01	1.25E+00	61-62	1.30E+01	8.13E-02
65-66	2.53E+01	1.02E+00	65-66	2.53E+01	2.44E+00	65-66	2.53E+01	1.58E-01
69-70	3.30E+01	1.33E+00	69-70	3.30E+01	3.18E+00	69-70	3.30E+01	2.06E-01
74-75	4.40E+01	1.77E+00	74-75	4.40E+01	4.23E+00	74-75	4.40E+01	2.75E-01
79-80	3.71E+02	1.49E+01	79-80	3.71E+02	3.57E+01	79-80	3.71E+02	2.32E+00
82-83	2.84E+03	1.14E+02	82-83	2.84E+03	2.73E+02	82-83	2.84E+03	1.77E+01
90	2.80E+04	1.13E+03	90	2.80E+04	2.70E+03	90	2.80E+04	1.75E+02
95-96	3.28E+04	1.32E+03	95-96	3.28E+04	3.15E+03	95-96	3.28E+04	2.05E+02
102-103	3.17E+04	1.27E+03	102-103	3.17E+04	3.05E+03	102-103	3.17E+04	1.98E+02
108-109	4.25E+04	1.71E+03	108-109	4.25E+04	4.09E+03	108-109	4.25E+04	2.66E+02
112	3.28E+04	1.32E+03	112	3.28E+04	3.16E+03	112	3.28E+04	2.05E+02
127.4	1.28E+04	5.15E+02	127.4	1.28E+04	1.23E+03	127.4	1.28E+04	8.01E+01
SX-113			SX-115			S-104		
Depth (ft) bgs	NO3 (ug/g soil)	NO3 (Kg)	Depth (ft) bgs	NO3 (ug/g soil)	NO3 (Kg)	Depth (ft) bgs	NO3 (ug/g soil)	NO3 (Kg)
33	1.00	2.28E-01	33	1.00	8.85E-02	33	1.00	3.89E-01
56.25	0.76	1.73E-01	56.25	0.76	6.73E-02	56.25	0.76	2.95E-01
57.5	3.10	7.06E-01	57.5	3.10	2.74E-01	57.5	3.10	1.21E+00
61.25	1.35	3.07E-01	61.25	1.35	1.19E-01	61.25	1.35	5.25E-01
62.75	5.25	1.20E+00	62.75	5.25	4.65E-01	62.75	5.25	2.04E+00
63.25	8.83	2.01E+00	63.25	8.83	7.81E-01	63.25	8.83	3.43E+00
63.75	11.34	2.58E+00	63.75	11.34	1.00E+00	63.75	11.34	4.41E+00
64.75	12.43	2.83E+00	64.75	12.43	1.10E+00	64.75	12.43	4.83E+00
68	19.93	4.54E+00	68	19.93	1.76E+00	68	19.93	7.75E+00
70	10.26	2.34E+00	70	10.26	9.08E-01	70	10.26	3.99E+00
71	27.85	6.34E+00	71	27.85	2.46E+00	71	27.85	1.08E+01
73.25	136.83	3.12E+01	73.25	136.83	1.21E+01	73.25	136.83	5.32E+01
73.75	400.86	9.13E+01	73.75	400.86	3.55E+01	73.75	400.86	1.56E+02
74.25	431.09	9.82E+01	74.25	431.09	3.81E+01	74.25	431.09	1.68E+02
75.25	321.44	7.32E+01	75.25	321.44	2.84E+01	75.25	321.44	1.25E+02
79.25	271.27	6.18E+01	79.25	271.27	2.40E+01	79.25	271.27	1.05E+02
79.75	275.95	6.28E+01	79.75	275.95	2.44E+01	79.75	275.95	1.07E+02
80.25	358.65	8.17E+01	80.25	358.65	3.17E+01	80.25	358.65	1.39E+02

Table E1.3. Vadose Zone Inventory Estimates for NO₃ for Individual Tanks (3 Sheets)

SX-113			SX-115			S-104		
Depth (ft) bgs	NO3 (ug/g soil)	NO3 (Kg)	Depth (ft) bgs	NO3 (ug/g soil)	NO3 (Kg)	Depth (ft) bgs	NO3 (ug/g soil)	NO3 (Kg)
87	73.51	1.67E+01	87	73.51	6.51E+00	87	73.51	2.86E+01
88.4	446.68	1.02E+02	88.4	446.68	3.95E+01	88.4	446.68	1.74E+02
95	340.37	7.75E+01	95	340.37	3.01E+01	95	340.37	1.32E+02
99	162.65	3.70E+01	99	162.65	1.44E+01	99	162.65	6.32E+01
100	423.71	9.65E+01	100	423.71	3.75E+01	100	423.71	1.65E+02
103.25	156.9	3.57E+01	103.25	156.9	1.39E+01	103.25	156.9	6.10E+01
105.25	75.31	1.72E+01	105.25	75.31	6.66E+00	105.25	75.31	2.93E+01
107	342.38	7.80E+01	107	342.38	3.03E+01	107	342.38	1.33E+02
116	467.69	1.07E+02	116	467.69	4.14E+01	116	467.69	1.82E+02
123.8			123.8			123.8		0.00E+00
124.35	864.67	1.97E+02	124.35	864.67	7.65E+01	124.35	864.67	3.36E+02
125.35	2179.74	4.96E+02	125.35	2179.74	1.93E+02	125.35	2179.74	8.47E+02
126.35	3304	7.52E+02	126.35	3304	2.92E+02	126.35	3304	1.28E+03
129.45	3932.54	8.96E+02	129.45	3932.54	3.48E+02	129.45	3932.54	1.53E+03
132.45	3195.73	7.28E+02	132.45	3195.73	2.83E+02	132.45	3195.73	1.24E+03
134.45	811.76	1.85E+02	134.45	811.76	7.18E+01	134.45	811.76	3.16E+02
136	2775.74	6.32E+02	136	2775.74	2.46E+02	136	2775.74	1.08E+03
138.2	2733.58	6.23E+02	138.2	2733.58	2.42E+02	138.2	2733.58	1.06E+03
140.65	2738.14	6.24E+02	140.65	2738.14	2.42E+02	140.65	2738.14	1.06E+03
141.65	2593.89	5.91E+02	141.65	2593.89	2.30E+02	141.65	2593.89	1.01E+03
142.75	2396.13	5.46E+02	142.75	2396.13	2.12E+02	142.75	2396.13	9.31E+02
144.2	1800.1	4.10E+02	144.2	1800.1	1.59E+02	144.2	1800.1	7.00E+02
145.65	1552.49	3.54E+02	145.65	1552.49	1.37E+02	145.65	1552.49	6.03E+02
146.65	2454.17	5.59E+02	146.65	2454.17	2.17E+02	146.65	2454.17	9.54E+02
147.55	761.89	1.74E+02	147.55	761.89	6.74E+01	147.55	761.89	2.96E+02
148.55	1385.37	3.16E+02	148.55	1385.37	1.23E+02	148.55	1385.37	5.39E+02
149.55	2140.04	4.87E+02	149.55	2140.04	1.89E+02	149.55	2140.04	8.32E+02
152.2	408.97	9.31E+01	152.2	408.97	3.62E+01	152.2	408.97	1.59E+02
153.15	229.2	5.22E+01	153.15	229.2	2.03E+01	153.15	229.2	8.91E+01
155.15	44.09	1.00E+01	155.15	44.09	3.90E+00	155.15	44.09	1.71E+01
156.1	292.81	6.67E+01	156.1	292.81	2.59E+01	156.1	292.81	1.14E+02
156.55	86.84	1.98E+01	156.55	86.84	7.68E+00	156.55	86.84	3.38E+01
157.75	3.56	8.11E-01	157.75	3.56	3.15E-01	157.75	3.56	1.38E+00
158.65	24.93	5.68E+00	158.65	24.93	2.21E+00	158.65	24.93	9.69E+00
159.75	32.24	7.34E+00	159.75	32.24	2.85E+00	159.75	32.24	1.25E+01
161	23.02	5.24E+00	161	23.02	2.04E+00	161	23.02	8.95E+00

Table E1.3. Vadose Zone Inventory Estimates for NO₃ for Individual Tanks (3 Sheets)

SX-113			SX-115			S-104		
Depth (ft) bgs	NO3 (ug/g soil)	NO3 (Kg)	Depth (ft) bgs	NO3 (ug/g soil)	NO3 (Kg)	Depth (ft) bgs	NO3 (ug/g soil)	NO3 (Kg)
162	28.29	6.44E+00	162	28.29	2.50E+00	162	28.29	1.10E+01
166	17.19	3.91E+00	166	17.19	1.52E+00	166	17.19	6.68E+00
167	11.36	2.59E+00	167	11.36	1.01E+00	167	11.36	4.42E+00
175	5.65	1.29E+00	175	5.65	5.00E-01	175	5.65	2.20E+00
185	3.87	8.81E-01	185	3.87	3.42E-01	185	3.87	1.50E+00
184.8	6.53	1.49E+00	184.8	6.53	5.78E-01	184.8	6.53	2.54E+00
186	0.78	1.78E-01	186	0.78	6.90E-02	186	0.78	3.03E-01
190	3.13	7.13E-01	190	3.13	2.77E-01	190	3.13	1.22E+00
194.55	1.14	2.60E-01	194.55	1.14	1.01E-01	194.55	1.14	4.43E-01
204.45	76.79	1.75E+01	204.45	76.79	6.80E+00	204.45	76.79	2.98E+01
205.1	25.29	5.76E+00	205.1	25.29	2.24E+00	205.1	25.29	9.83E+00

Table E1.4. Vadose Zone Inventory Estimates for Cr for Individual Tanks (3 Sheets)

SX-107			SX-108			SX-109		
Depth (ft) bgs	Cr (ug/g soil)	Cr (Kg)	Depth (ft) bgs	Cr (ug/g soil)	Cr (Kg)	Depth (ft) bgs	Cr (ug/g soil)	Cr (Kg)
25-26	5.00E-04	8.09E-05	25-26	5.00E-04	1.94E-04	25-26	5.00E-04	1.26E-05
44-45	2.89E-03	4.68E-04	44-45	2.89E-03	1.12E-03			
56-57	3.42E-03	5.53E-04	56-57	3.42E-03	1.33E-03	56-57	3.42E-03	8.61E-05
61-62	8.15E-03	1.32E-03	61-62	8.15E-03	3.16E-03	61-62	8.15E-03	2.05E-04
65-66	3.43E-01	5.54E-02	65-66	3.43E-01	1.33E-01	65-66	3.43E-01	8.63E-03
69-70	5.07E+00	8.20E-01	69-70	5.07E+00	1.97E+00	69-70	5.07E+00	1.28E
74-75	4.09E+00	6.62E-01	74-75	4.09E+00	1.59E+00	74-75	4.09E+00	1.03E-01
79-80	7.17E-01	1.16E-01	79-80	7.17E-01	2.78E-01	79-80	7.17E-01	1.81E-02
82-83	7.45E+02	1.21E+02	82-83	7.45E+02	2.89E+02	82-83	7.45E+02	1.88E+01
90	7.12E+02	1.15E+02	90	7.12E+02	2.76E+02	90	7.12E+02	1.79E+01
95-96	2.60E+02	4.21E+01	95-96	2.60E+02	1.01E+02	95-96	2.60E+02	6.55E+00
102-103	5.28E+02	8.54E+01	102-103	5.28E+02	2.05E+02	102-103	5.28E+02	1.33E+01
108-109	4.81E+02	7.78E+01	108-109	4.81E+02	1.87E+02	108-109	4.81E+02	1.21E+01
112	1.75E+02	2.83E+01	112	1.75E+02	6.79E+01	112	1.75E+02	4.41E+00
127.4	1.15E-02	1.86E-03	127.4	1.15E-02	4.46E-03	127.4	1.15E-02	2.90E-04
SX-113			SX-115			S-104		
Depth (ft) bgs	Cr (ug/g soil)	Cr (Kg)	Depth (ft) bgs	Cr (ug/g soil)	Cr (Kg)	Depth (ft) bgs	Cr (ug/g soil)	Cr (Kg)
33	2.50E-03	1.46E-02	33	2.50E-03	1.45E-02	33	2.50E-03	2.25E-02
56.25	5.00E-04	2.92E-03	56.25	5.00E-04	2.89E-03	56.25	5.00E-04	4.49E-03
57.5	5.00E-04	2.92E-03	57.5	5.00E-04	2.89E-03	57.5	5.00E-04	4.49E-03
61.25	5.13E-04	2.99E-03	61.25	5.13E-04	2.96E-03	61.25	5.13E-04	4.60E-03
62.75	5.01E-04	2.92E-03	62.75	5.01E-04	2.89E-03	62.75	5.01E-04	4.49E-03
63.25	1.44E-03	8.38E-03	63.25	1.44E-03	8.30E-03	63.25	1.44E-03	1.29E-02
63.75	1.29E-03	7.54E-03	63.75	1.29E-03	7.46E-03	63.75	1.29E-03	1.16E-02
64.75	5.02E-04	2.93E-03	64.75	5.02E-04	2.90E-03	64.75	5.02E-04	4.51E-03
68	1.67E-02	9.77E-02	68	1.67E-02	9.67E-02	68	1.67E-02	1.50E-01
70	3.02E-02	1.76E-01	70	3.02E-02	1.75E-01	70	3.02E-02	2.71E-01
71	5.01E-01	2.93E+00	71	5.01E-01	2.90E+00	71	5.01E-01	4.50E+00
73.25	1.56E+00	9.12E+00	73.25	1.56E+00	9.03E+00	73.25	1.56E+00	1.40E+01
73.75	5.00E+00	2.92E+01	73.75	5.00E+00	2.89E+01	73.75	5.00E+00	4.49E+01
74.25	6.85E+00	4.00E+01	74.25	6.85E+00	3.96E+01	74.25	6.85E+00	6.15E+01
75.25	3.16E+00	1.85E+01	75.25	3.16E+00	1.83E+01	75.25	3.16E+00	2.84E+01
79.25	3.63E+00	2.12E+01	79.25	3.63E+00	2.10E+01	79.25	3.63E+00	3.26E+01
79.75	2.72E+00	1.59E+01	79.75	2.72E+00	1.58E+01	79.75	2.72E+00	2.45E+01

Table E1.4. Vadose Zone Inventory Estimates for Cr for Individual Tanks (3 Sheets)

SX-113			SX-115			S-104		
Depth (ft) bgs	Cr (ug/g soil)	Cr (Kg)	Depth (ft) bgs	Cr (ug/g soil)	Cr (Kg)	Depth (ft) bgs	Cr (ug/g soil)	Cr (Kg)
87	4.13E-01	2.41E+00	87	4.13E-01	2.39E+00	87	4.13E-01	3.71E+00
88.4	6.47E+00	3.78E+01	88.4	6.47E+00	3.74E+01	88.4	6.47E+00	5.81E+01
95	3.77E+00	2.20E+01	95	3.77E+00	2.18E+01	95	3.77E+00	3.39E+01
99	1.84E+00	1.07E+01	99	1.84E+00	1.06E+01	99	1.84E+00	1.65E+01
100	7.51E+00	4.39E+01	100	7.51E+00	4.34E+01	100	7.51E+00	6.74E+01
103.25	2.61E+00	1.52E+01	103.25	2.61E+00	1.51E+01	103.25	2.61E+00	2.34E+01
105.25	1.32E+00	7.69E+00	105.25	1.32E+00	7.62E+00	105.25	1.32E+00	1.18E+01
107	8.15E+00	4.76E+01	107	8.15E+00	4.71E+01	107	8.15E+00	7.31E+01
116	6.85E+00	4.00E+01	116	6.85E+00	3.96E+01	116	6.85E+00	6.15E+01
123.8	7.30E+00	4.26E+01	123.8	7.30E+00	4.22E+01	123.8	7.30E+00	6.55E+01
124.35	7.30E+00	4.26E+01	124.35	7.30E+00	4.22E+01	124.35	7.30E+00	6.55E+01
125.35	6.27E+00	3.66E+01	125.35	6.27E+00	3.63E+01	125.35	6.27E+00	5.63E+01
126.35	3.62E-01	2.12E+00	126.35	3.62E-01	2.09E+00	126.35	3.62E-01	3.25E+00
129.45	4.30E-03	2.51E-02	129.45	4.30E-03	2.49E-02	129.45	4.30E-03	3.86E-02
132.45	5.01E-04	2.93E-03	132.45	5.01E-04	2.90E-03	132.45	5.01E-04	4.50E-03
134.45	4.04E-04	2.36E-03	134.45	4.04E-04	2.34E-03	134.45	4.04E-04	3.63E-03
136	2.50E-03	1.46E-02	136	2.50E-03	1.45E-02	136	2.50E-03	2.24E-02
138.2	2.50E-03	1.46E-02	138.2	2.50E-03	1.45E-02	138.2	2.50E-03	2.25E-02
140.65	2.50E-03	1.46E-02	140.65	2.50E-03	1.45E-02	140.65	2.50E-03	2.24E-02
141.65	2.50E-03	1.46E-02	141.65	2.50E-03	1.45E-02	141.65	2.50E-03	2.25E-02
142.75	1.05E-03	6.16E-03	142.75	1.05E-03	6.10E-03	142.75	1.05E-03	9.47E-03
144.2	8.57E-04	5.01E-03	144.2	8.57E-04	4.96E-03	144.2	8.57E-04	7.70E-03
145.65	2.50E-03	1.46E-02	145.65	2.50E-03	1.44E-02	145.65	2.50E-03	2.24E-02
146.65	9.63E-04	5.62E-03	146.65	9.63E-04	5.57E-03	146.65	9.63E-04	8.64E-03
147.55	1.47E-04	8.58E-04	147.55	1.47E-04	8.50E-04	147.55	1.47E-04	1.32E-03
148.55	1.48E-03	8.66E-03	148.55	1.48E-03	8.57E-03	148.55	1.48E-03	1.33E-02
149.55	2.50E-03	1.46E-02	149.55	2.50E-03	1.45E-02	149.55	2.50E-03	2.24E-02
152.2	9.33E-04	5.45E-03	152.2	9.33E-04	5.39E-03	152.2	9.33E-04	8.37E-03
153.15	6.76E-04	3.95E-03	153.15	6.76E-04	3.91E-03	153.15	6.76E-04	6.07E-03
155.15	5.00E-04	2.92E-03	155.15	5.00E-04	2.89E-03	155.15	5.00E-04	4.49E-03
156.1	1.04E-03	6.08E-03	156.1	1.04E-03	6.02E-03	156.1	1.04E-03	9.34E-03
156.55	2.50E-03	1.46E-02	156.55	2.50E-03	1.45E-02	156.55	2.50E-03	2.25E-02
157.75	5.08E-04	2.97E-03	157.75	5.08E-04	2.94E-03	157.75	5.08E-04	4.56E-03
158.65	1.02E-03	5.95E-03	158.65	1.02E-03	5.89E-03	158.65	1.02E-03	9.14E-03
159.75	5.42E-03	3.17E-02	159.75	5.42E-03	3.13E-02	159.75	5.42E-03	4.87E-02
161	2.96E-03	1.73E-02	161	2.96E-03	1.71E-02	161	2.96E-03	2.65E-02

Table E1.4. Vadose Zone Inventory Estimates for Cr for Individual Tanks (3 Sheets)

SX-113			SX-115			S-104		
Depth (ft) bgs	Cr (ug/g soil)	Cr (Kg)	Depth (ft) bgs	Cr (ug/g soil)	Cr (Kg)	Depth (ft) bgs	Cr (ug/g soil)	Cr (Kg)
162	4.37E-03	2.55E-02	162	4.37E-03	2.53E-02	162	4.37E-03	3.92E-02
166	1.23E-03	7.19E-03	166	1.23E-03	7.12E-03	166	1.23E-03	1.11E-02
167	6.00E-04	3.51E-03	167	6.00E-04	3.47E-03	167	6.00E-04	5.39E-03
175	2.36E-04	1.38E-03	175	2.36E-04	1.36E-03	175	2.36E-04	2.12E-03
185	1.01E-03	5.87E-03	185	1.01E-03	5.81E-03	185	1.01E-03	9.03E-03
184.8	7.09E-04	4.14E-03	184.8	7.09E-04	4.10E-03	184.8	7.09E-04	6.37E-03
186			186			186		
190	1.47E-04	8.59E-04	190	1.47E-04	8.51E-04	190	1.47E-04	1.32E-03
194.55	5.41E-04	3.16E-03	194.55	5.41E-04	3.13E-03	194.55	5.41E-04	4.86E-03
204.45	5.00E-04	2.92E-03	204.45	5.00E-04	2.89E-03	204.45	5.00E-04	4.49E-03
205.1	5.72E-04	3.34E-03	205.1	5.72E-04	3.31E-03	205.1	5.72E-04	5.14E-03

ATTACHMENT E2

INVENTORY DISTRIBUTIONS

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E2, 0 UNIFORM INITIAL INVENTORY DISTRIBUTIONS

Color-scaled images of the uniform ~~initial~~ inventory distributions for the contaminant species (i.e., cesium-137, technetium-99, chromium, and nitrate) are shown in Figures E2.1 through E2.12 for cross-sections SX-DD', SX-FF', and S-CC'. The uniform inventory distributions conserve both the concentration and integrated mass records for each elevation bin by varying the distribution radius. Inventories are assumed to be distributed at each grid elevation as a circular disk.

Figure E2.1. Initial Cs-137 Aqueous-Phase Concentration, Uniform Distribution, Cross-Section SX-DD' (SX-107, -108, -109)

Figure E2.2. Initial Tc-99 Aqueous-Phase Concentration, Uniform Distribution, Cross-Section SX-DD' (SX-107, -108, -109)

Figure E2.3. Initial Cr Aqueous-Phase Concentration, Uniform Distribution, Cross-section SX-DD' (SX-107, -108, -109)

Figure E2.4. Initial NO₃ Aqueous-Phase Concentration, Uniform Distribution, Cross-section SX-DD' (SX-107, -108, -109)

Figure E2.5. Initial Cs-137 Aqueous-Phase Concentration, Uniform Distribution, Cross-Section SX-FF' (SX-113, -114, -115)

Figure E2.6. Initial Tc-99 Aqueous-Phase Concentration, Uniform Distribution, Cross-Section SX-FF' (SX-113, -114, -115)

Figure E2.7. Initial Cr Aqueous-Phase Concentration, Uniform Distribution, Cross-Section SX-FF' (SX-113,-114,-115)

Figure E2.8. Initial NO₃ Aqueous-Phase Concentration, Uniform Distribution, Cross-Section SX-FF' (SX-113,-114,-115)

Figure E2.9. Initial Cs-137 Aqueous-Phase Concentration, Uniform Distribution, Cross-Section S-CC' (S-104, -105, -106)

Figure E2.10. Initial Tc-99 Aqueous-Phase Concentration, Uniform Distribution, Cross-Section S-CC' (S-104, -105, -106)

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Figure E2.12. Initial NO₃ Aqueous-Phase Concentration, Uniform Distribution, Cross-Section S-CC' (S-104, -105, -106)

E2.2.0 NONUNIFORM INITIAL INVENTORY DISTRIBUTIONS

Color-scaled images of the nonuniform initial inventory distributions for the contaminant species (i.e., cesium-137, technetium-99, chromium, and nitrate) are shown in Figures E2.13 through E2.24 for cross-sections SX-DD', SX-FF', and S-CC'. The nonuniform inventory distributions conserve the integrated mass records for each elevation, but with a localized concentration. Inventory concentrations are generally higher than the concentration records at each elevation. Inventories are assumed to be distributed at each grid elevation as a circular disk.

Figure E2.13. Initial Cs-137 Aqueous-Phase Concentration, Nonuniform Distribution, Cross-Section SX-DD' (SX-107, -108, -109)

Figure E2.14. Initial Tc-99 Aqueous-Phase Concentration, Nonuniform Distribution, Cross-Section SX-DD' (SX-107, -108, -109)

Figure E2.15. Initial Cr Aqueous-Phase Concentration, Nonuniform Distribution, Cross-Section SX-DD' (SX-107, -108, -109)

Figure E2.16. Initial NO₃ Aqueous-Phase Concentration, Nonuniform Distribution, Cross-Section SX-DD' (SX-107, -108, -109)

Figure E2.17. Initial Cs-137 Aqueous-Phase Concentration, Nonuniform Distribution, Cross-Section SX-FF' (SX-113, -114, -115)

Figure E2.18. Initial Tc-99 Aqueous-Phase Concentration, Nonuniform Distribution, Cross-Section SX-FF' (SX-113, -114, -115)

Figure E2.19. Initial Cr Aqueous-Phase Concentration, Nonuniform Distribution, Cross-Section SX-FF' (SX-113, -114, -115)

Figure E2.20. Initial NO₃ Aqueous-Phase Concentration, Nonuniform Distribution, Cross Section SX-FF' (SX-113, -114, -115)

Figure E2.21. Initial Cs-137 Aqueous-Phase Concentration, Nonuniform Distribution, Cross-section S-CC' (S-104, -105, -106)

Figure E2.22. Initial Tc-99 Aqueous-Phase concentration, Nonuniform Distribution, Cross-Section S-CC' (S-104, -105, -106)

Figure E2.23. Initial Cr Aqueous-Phase Concentration, Nonuniform Distribution, Cross-section S-CC' (S-104, -105, -106)

Figure E2.24. Initial NO₃ Aqueous-Phase Concentration, Nonuniform Distribution, Cross-section S-CC' (S-104, -105, -106)

E2.3.0 DISPLACED INITIAL INVENTORY DISTRIBUTIONS

Color-scaled images of the displaced initial inventory distributions for the contaminant species (i.e., cesium-137, technetium-99, chromium, and nitrate) are shown in Figures E2.25 through E2.36 for cross-sections SX-DD', SX-FF', and S-CC'. The displaced inventory distributions conserve the integrated mass records for each elevation, but with a localized and displaced concentration. Inventory concentrations are generally higher than the concentration records at each corresponding undisplaced elevation. Inventories are assumed to be distributed at each grid elevation as a circular disk.

Figure E2.25. Initial Cs-137 Aqueous-Phase Concentration, Displaced Distribution, Cross-Section SX-DD' (SX-107, -108, -109)

Figure E2.26. Initial Tc-99 Aqueous-Phase Concentration, Displaced Distribution, Cross-Section SX-DD' (SX-107, -108, -109)

Figure E2.27. Initial Cr Aqueous-Phase Concentration, Displaced Distribution, Cross-Section SX-DD' (SX-107, -108, -109)

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Figure E2.35. Initial Cr Aqueous-Phase Concentration, Displaced Distribution, Cross-section S-CC' (S-104, -105, -106)

Figure E2.36. Initial NO₃ Aqueous-Phase Concentration, Displaced Distribution, Cross-Section S-CC' (S-104, -105, -106)

E2.4.0 ALTERNATE INITIAL INVENTORY DISTRIBUTIONS

Color-scaled images of the alternate initial inventory distributions for the contaminant species (i.e., cesium-137, technetium-99, chromium, and nitrate) are shown in Figures E2.37 through E2.48 for cross-sections SX-DD', SX-FF', and S-CC'. The alternate inventory distributions **only** conserve the integrated mass records for each elevation bin. The concentration is computed based on distribution radius and integrated mass for the elevation bin. Inventories are assumed to be distributed at each grid elevation **as** a circular disk.

Figure E2.37. Initial Cs-137 Aqueous-Phase Concentration, Alternate Distribution, Cross-Section SX-DD' (SX-107, -108, -109)

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Figure E2.48. Initial NO₃ Aqueous-Phase Concentration, Alternate Distribution, Cross-Section S-CC' (S-104, -105, -106)

ATTACHMENT E3

VADOSE ZONE AND UNCONFINED
AQUIFER MODELING RESULTS

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E3.1.0 CASE 1: BASE CASE (*NO ACTION ALTERNATIVE*)

This scenario involves simulating flow **and** transport for cross-sections through tanks (a) SX-107, -108, **and** -109; (b) SX-113, -114, **and** -115; **and** (c) S-104, -105, and -106 considering natural infiltration only, no water-line leak, no interim barrier **and** a closure barrier by the year 2040.

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Figure E3.2. Case 1 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104,-105,-106)

Figure E3.3. Case 1 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section S-CC' (S-104, -105, -106)

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Figure E3.13. Case 1 Area-Weighted Average Tc-99 Concentration and Dose versus Time at Compliance Points

Figure E3.14. Case 1 Area-Weighted Average Cr Concentration versus Time at Compliance Points

Figure E3.15. Case 1 Area-Weighted Average NO₃ Concentration versus Time at Compliance Points

E3.2.0 CASE 2: BARRIER ALTERNATIVE AND NO WATER-LINE LEAKS

This scenario involves simulating flow and transport for cross-sections through tanks (a) SX-107, -108, and -109; (b) SX-113, -114, and -115; and (c) S-104, -105, and -106 considering placement of an interim barrier by 2010, a closure barrier by 2040 (i.e., the interim barrier replaced by the closure barrier), and no water-line leak.

Figure E3.16. Case 2 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.17. Case 2 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.18. Case 2 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.19. Case 2 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.20. Case 2 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.21. Case 2 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.22. Case 2 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.23. Case 2 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.24. Case 2 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.25. Case 2 Aqueous Flux versus Time at the Water Table for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.26. Case 2 Aqueous Flux versus Time at the Water Table for Cross-Section SX-DD' (S-107, -108, -109)

Figure E3.27. Case 2 Aqueous Flux versus Time at the Water Table for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.29. Case 2 Area-Weighted Average Cr Concentration versus Time at Compliance Points

E3.3.0 CASE 3: NO BARRIER AND WATER-LINE LEAK (25,000 IN 5 DAYS)

This scenario involves simulating flow and transport for cross-sections through tanks (a) **SX-107, -108, and -109**; (b) **SX-113, -114, and -115**; and (c) **S-104, -105, and -106** considering natural infiltration, water-line leak (25,000gal in 5 days) for tank **SX-115** only, and no barrier until closure in **2040**.

Figure E3.31. Case 3 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.32. Case 3 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.33. Case 3 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.34. Case 3 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.35. Case 3 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.36. Case 3 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.37. Case 3 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.38. Case 3 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section SX-FF' (SX-113, -114, -115)

Figure E3.39. Case 3 NO₃ Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.40. Case 3 Aqueous Flux versus Time at the Water Table for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.41. Case 3 Aqueous Flux versus Time at the Water Table for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.42. Case 3 Aqueous Flux versus Time at the Water Table for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.45. Case 3 Area-Weighted Average NO₃ Concentration versus Time at Compliance Points

E3.4.0 CASE 4: NO BARRIER AND CLASTIC DIKES

This scenario involves simulating flow and transport for cross-sections through tanks (a) SX-107, -108, and -109; (b) **SX**-113, -114, and -115; and (c) S-104, -105, and -106 considering natural infiltration, clastic dikes between tanks SX-107, -108, and -109, and no barrier until closure in 2040.

Figure E3.46. Case 4 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section S-CC' (S-104, -105, -106)

Figure E3.47. Case 4 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.48. Case 4 NO₃ Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.49. Case 4 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.52. Case 4 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section SX-FF' (SX-113, -114, -115)

Figure E3.53. Case 4 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section SX-FF' (SX-113, -114, -115)

Figure E3.54. Case 4 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.55. Case 4 Aqueous Flux versus Time at the Water Table for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.56. Case 4 Aqueous Flux versus Time at the Water Table for Cross-section SX-DD' (SX-107, -108, -109)

Figure E3.57. Case 4 Aqueous Flux versus Time at the Water Table for Cross-section SX-FF' (SX-113, -114, -115)

Figure E3.58. Case 4 Area-Weighted Average Tc-99 Concentration and Dose versus Time at Compliance Points

Figure E3.59. Case 4 Area-Weighted Average Cr Concentration versus Time at Compliance Points

Figure E3.60. Case 4 Area-Weighted Average NO_3 Concentration versus Time at Compliance Points

E3.5.0 CASE 5: NONUNIFORM INVENTORY DISTRIBUTION AND NO BARRIER

This scenario involves simulating flow and transport for cross-sections through tanks (a) SX-107, -108, **and** -109; (b) SX-113, -114, **and** -115; and (c) S-104, -105, and -106 considering natural infiltration only, no water-line leak, no barrier until closure in 2040, and a higher distribution of inventory at a few locations (e.g., a few nodes, with a high concentration, either at the same depth or at different locations).

Figure E3.61. Case 5 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.62. Case 5 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.63. Case 5 NO₃ Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.64. Case 5 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.65. Case 5 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section SX-DD' (SX-107, -108, -109)

Figure E3.66. Case 5 NO₃ Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.67. Case 5 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section SX-FF' (SX-113, -114, -115)

Figure E3.68. Case 5 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section SX-FF' (SX-113, -114, -115)

Figure E3.69. Case 5 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.70. Case 5 Aqueous Flux versus Time at the Water Table for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.71. Case 5 Aqueous Flux versus Time at the Water Table for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.72. Case 5 Aqueous Flux versus Time at the Water Table for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.73. Case 5 Area-Weighted Average Tc-99 Concentration versus Time at the Compliance Points

Figure E3.74. Case 5 Area-Weighted Average Cr Concentration versus Time at the Compliance Points

Figure E3.75. Case 5 Area-Weighted Average NO_3 Concentration versus Time at the Compliance Points

E3.6.0 CASE 6: NONUNIFORM INVENTORY DISTRIBUTION AND BARRIER

This scenario involves simulating flow and transport for cross-sections through tanks (a) SX-107, -108, and -109; (b) SX-113, -114, and -115; and (c) S-104, -105, and -106 considering barrier infiltration (interim barrier replaced at closure in 2040), no water-line leak, and a higher distribution of inventory at a few locations (e.g., a few nodes, with a high concentration, either at the same depth or at different locations).

Figure E3.76. Case 6 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.77. Case 6 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.78. Case 6 NO₃ Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.80. Case 6 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section SX-DD' (SX-107, -108, -109)

Figure E3.81. Case 6 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.82. Case 6 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section SX-FF' (SX-113, -114, -115)

Figure E3.83. Case 6 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.84. Case 6 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section SX-FF' (SX-113, -114, -115)

Figure E3.85. Case 6 Aqueous Flux versus Time at the Water Table for Cross-section S-CC' (S-104, -105, -106)

Figure E3.86. Case 6 Aqueous Flux versus Time at the Water Table for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.87. Case 6 Aqueous Flux versus Time at the Water Table for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.89. Case 6 Area-Weighted Average Cr Concentration versus Time at the Compliance Points

Figure E3.90. Case 6 Area-Weighted Average NO_3 Concentration versus Time at the Compliance Points

E3.7.0 CASE 7: LOCATION OF INVENTORY DISTRIBUTION AND NO BARRIER

This scenario involves simulating flow and transport for cross-sections through tanks (a) SX-107, -108, and -109; (b) SX-113, -114, and -115; and (c) S-104, -105, and -106 considering natural infiltration only, no water-line leak, no barrier until closure in 2040, and concentrated distribution of inventory location close to the water table.

Figure E3.91. Case 7 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.92. Case 7 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.93. Case 7 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section S-CC' (S-104, -105, -106)

Figure E3.94. Case 7 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section SX-DD' (SX-107, -108, -109)

Figure E3.95. Case 7 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section SX-DD' (SX-107, -108, -109)

Figure E3.96. Case 7 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section SX-DD' (SX-107, -108, -109)

Figure E3.97. Case 7 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.98. Case 7 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.99. Case 7 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section SX-FF' (SX-113, -114, -115)

Figure E3.100. Case 7 Aqueous Flux versus Time at the Water Table for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.102. Case 7 Aqueous Flux versus Time at the Water Table for Cross-section SX-FF' (SX-113, -114, -115)

Figure E3.103. Case 7 Area-Weighted Average Tc-99 Concentration versus Time at the Compliance Points

Figure E3.104. Case 7 Area-Weighted Average Cr Concentration versus Time at the Compliance Points

Figure E3.105. Case 7 Area-Weighted Average NO_3 Concentration versus Time at the Compliance Points

E3.8.0 CASE 8: DENSITY AND VISCOSITY EFFECTS

This scenario involves simulating flow and transport for cross-sections through *tanks* (a) **SX-107, -108, and -109**; (b) **SX-113, -114, and -115**; and (c) **S-104, -105, and -106** considering natural infiltration only, no water-line leak, enhanced density and viscosity, no barrier until closure in **2040**, and a uniform inventory distribution.

Figure E3.106. Case 8 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section S-CC' (S-104, -105, -106)

Figure E3.107. Case 8 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section S-CC' (S-104, -105, -106)

Figure E3.108. Case 8 NO₃ Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.109. Case 8 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.110. Case 8 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.111. Case 8 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section SX-DD' (SX-107, -108, -109)

Figure E3.112. Case 8 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.113. Case 8 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.114. Case 8 NO₃ Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.115. Case 8 Aqueous Flux versus Time at the Water Table for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.116. Case 8 Aqueous Flux versus Time at the Water Table for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.117. Case 8 Aqueous Flux versus Time at the Water Table for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.119. Case 8 Area-Weighted Average Cr Concentration versus Time at the Compliance Points

Figure E3.120. Case 8 Area-Weighted Average NO_3 Concentration versus Time at the Compliance Points

E3.9.0 CASE 9: BASE CASE (50 MM/YR METEORIC RECHARGE)

This scenario involves simulating flow and transport for cross-sections through tanks (a) SX-107, -108, and -109; (b) SX-113, -114, and -115; and (c) S-104, -105, and -106 considering natural infiltration only at 50 mm/yr, no water-line leak, no interim barrier, a closure barrier by the year 2040, and a uniform inventory distribution.

Figure E3.121. Case 9 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.122. Case 9 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.123. Case 9 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.124. Case 9 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.125. Case 9 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.127. Case 9 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.128. Case 9 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.129. Case 9 NO₃ Concentration versus Time at the First Compliance Point (Le., Waste Management Area S-SX) for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.130. Case 9 Aqueous Flux versus Time at the Water Table for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.131. Case 9 Aqueous Flux versus Time at the Water Table for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.132. Case 9 Aqueous Flux versus Time at the Water Table for Cross-Section SX-FF' (SX-113, -114, -115)

E3.10.0 CASE 10: BASE CASE (30 MM/YR METEORIC RECHARGE)

This scenario involves simulating flow and transport for cross-sections through tanks (a) SX-107, -108, and -109; (b) SX-113, -114, and -115; and (c) S-104, -105, **and** -106 considering natural infiltration only at 30 mm/yr, no water-line leak, no interim barrier, a closure barrier by the year 2040, and a uniform inventory distribution.

Figure E3.136. Case 10 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.137. Case 10 Cr Concentration versus Time at the First Compliance Point (Le., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.138. Case 10 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.139. Case 10 Tc-99 Concentration versus Time at the First Compliance Point (Le., Waste Management Area S-SX) for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.140. Case 10 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.142. Case 10 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section SX-FF' (SX-113,-114,-115)

Figure E3.143. Case 10 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section SX-FF' (SX-113,-114,-115)

Figure E3.144. Case 10 NO_3 Concentration versus Time at the First Compliance Point (Le., Waste Management Area S-SX) for Cross-section SX-FF' (SX-113, -114, -115)

Figure E3.145. Case 10 Aqueous Flux versus Time at the Water Table for Cross-section S-CC' (S-104, -105, -106)

Figure E3.146. Case 10 Aqueous Flux versus Time at the Water Table for Cross-Section SX-DD' (SX-107,-108,-109)

Figure E3.147. Case 10 Aqueous Flux versus Time at the Water Table for Cross-Section SX-FF' (SX-113,-114,-115)

E3.11.0 CASE 11: BASE CASE (10 MM/YR METEORIC RECHARGE)

This scenario involves simulating flow and transport for cross-sections through tanks (a) SX-107, -108, and -109; (b) SX-113, -114, and -115; and (c) S-104, -105, and **-106** considering natural infiltration only at 10 mm/yr, no water-line leak, no interim barrier, a closure barrier by the year **2040**, and a uniform inventory distribution.

Figure E3.151. Case 11 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.152. Case 11 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.153. Case 11 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.155. Case 11 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.156. Case 11 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section SX-DD' (SX-107, -108, -109)

Figure E3.157. Case 11 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.158. Case 11 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-FF' (SX-113, -114, -115)

Figure E3.159. Case 11 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-section SX-FF' (SX-113, -114, -115)

Figure E3.160. Case 11 Aqueous Flux versus Time at the Water Table for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.161. Case 11 Aqueous Flux versus Time at the Water Table for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.163. Case 11 Area-Weighted Average Tc-99 Concentration versus Time at the Compliance Points

Figure E3.164. Case 11 Area-Weighted Average Cr Concentration versus Time at the Compliance Points

E3.12.0 CASE 12: ALTERNATE UNIFORM INVENTORY DISTRIBUTION

This scenario involves simulating flow and transport for cross-sections through tanks (a) SX-107, -108, and -109; (b) SX-113, -114, and -115; and (c) S-104, -105, and -106 considering natural infiltration only at 100mm/yr, no water-line leak, no interim barrier, a closure barrier by the year 2040, and an alternate uniform inventory distribution.

Figure E3.166. Case 12 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.167. Case 12 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.168. Case 12 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section S-CC' (S-104, -105, -106)

Figure E3.169. Case 12 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.170. Case 12 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.171. Case 12 NO_3 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-DD' (SX-107, -108, -109)

Figure E3.172. Case 12 Tc-99 Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-FF' (SX-113,-114,-115)

Figure E3.173. Case 12 Cr Concentration versus Time at the First Compliance Point (i.e., Waste Management Area S-SX) for Cross-Section SX-FF' (SX-113,-114,-115)

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ATTACHMENT E4

SOLUTE TRANSPORT TIME SEQUENCES

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ATTACHMENT E5

RECHARGE SENSITIVITY MODELING RESULTS

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APPENDIX F

**COST AND IMPLEMENTABILITY OF
INTERIM MEASURES AND
INTERIM CORRECTIVE MEASURES**

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LIST OF TERMS

ICM	interim corrective measure
WMA	waste management area

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F.I.O INTRODUCTION

This "Cost And Implementability of Interim Measures and Interim Corrective Measures" appendix describes the interim measures and interim corrective measures (ICMs) that have been evaluated as they relate to the waste management area (WMA) S-SX. Interim measures are initial response actions that can be taken while characterization activities are underway and long-term strategies are being developed to reduce the impacts of tank leaks on groundwater. Interim measures do not require comprehensive evaluation in a corrective measures study. ICMs are response actions having the objective of reducing contaminant migration to groundwater to acceptable regulatory levels and which require a balancing of risk, benefits, and costs.

Interim measure response actions that have been studied are discussed and how these interim measures are being implemented is addressed. Interim measures identified to date focus on actions to minimize infiltration and contaminant migration to groundwater. This appendix also provides estimated costs for implementing the interim measures at WMA S-SX as reflected in *Engineering Report, Single-Shell Tank Farms Interim Measures to Limit Infiltration Through the Vadose Zone* (Anderson 2001).

In general, ICMs involve a substantial commitment of resources, require a more thorough evaluation, and are intended to provide a more permanent solution to the long-term threats posed by a release. For those measures where engineering studies have been performed, results from those studies will be summarized. For other potential ICMs, it is premature to provide a detailed discussion of the associated cost and implementability issues. Detailed evaluation of the ICMs will be undertaken in a corrective measures study, or an accelerated corrective measures study pending results of this field investigation report.

F.2.0 INTERIM MEASURES

The engineering report (Anderson 2001) was prepared to assess potential measures to limit infiltration through the vadose zone at the single-shell tank farms. That study evaluates leaking water lines, wells within the single-shell tank farms, and surface water (both recharge and run-on). Included in this study are a number of interim measures that are 'good housekeeping' actions, which should be considered for implementation because they would reduce water infiltration at the tank farms and limit the migration of contamination through the vadose zone. The recommended interim measures include the following:

- Abandoning all active water lines within and near the tank farms
- Decommissioning unfit-for-use wells within the tank farms
- Establishing control measures to prevent water from running onto the tank farm from outside the fence.

These three measures could be implemented without a detailed technical evaluation. Summaries of the work that has been performed in these areas are provided in the following sections.

F.2.1 ABANDONING ACTIVE WATER LINES

Combined, the S and SX tank farms have approximately **1,930 m** (6,300 ft) of active water lines that have been abandoned to eliminate persistent leaks and prevent future water line breaks. These lines were mainly installed during original tank farm construction and have exceeded their design life.

F.2.2 DECOMMISSIONING UNFIT-FOR-USE WELLS

Wells that are unfit for use are potential preferential pathways for contaminant migration to reach the groundwater. The engineering report (Anderson 2001) identifies a number of wells in the S and SX tank farms that should be decommissioned.

F.2.3 BERMES

Run-on control consists of berms, ditches, and asphalt curbs constructed outside the water control area to prevent surface water outside the tank farm from flowing on the tank farm areas. The engineering report (Anderson 2001) recommends that, regardless of which interim measures are selected to reduce infiltration within the WMA, run-on control be established to prevent surface water from entering the WMA from outside sources. Run-on controls have been constructed at the S, SX, T, TX, TY, and U tank farms.

F.3.0 INTERIM CORRECTIVE MEASURES

ICMs have the same overall purpose as interim measures. Because of their size, complexity, or impact to operations, a more careful study must be performed before ICMs are implemented. Many potential ICMs have been identified; however, it is recognized that some of these potential ICMs are likely to be implemented sooner than others. Thus, this section describes the two sets of ICMs separately.

F.3.1 IDENTIFICATION OF POTENTIAL NEAR-TERM INTERIM CORRECTIVE MEASURES

The activities that have been undertaken to identify potential ICMs for the WMAs are described below.

- In 1992 an engineering study that evaluated 4 approaches for reducing surface infiltration at the WMAs (Young et al. 1992) was completed. The approaches evaluated were (1) polymer-modified asphalt, (2) fine-soil cover, (3) buildings (structures), and (4) flexible membrane liners. The engineering study concluded that implementation of these approaches for all of the WMAs ranged from \$40 million to \$158 million. Cost and other factors were the reasons that none of the approaches were implemented.
- On May 4 through 6, 1999 an innovative treatment remediation demonstration forum was held in Richland, Washington to discuss techniques for reducing and monitoring infiltration at the single-shell tank farms. The U.S. Department of Energy, Hanford Site contractors and various vendors from throughout the United States and Canada attended. Pacific Northwest National Laboratory summarized this conference in a two-volume report, *Reducing Water Infiltration Around Hanford Tanks* (Molton 1999). Four technical sessions were conducted to discuss (1) moisture monitoring and characterization, (2) structures or buildings to cover the WMAs, (3) surface modifications or covers, and (4) near-surface modifications (barriers and permeability reduction techniques). The forum concluded that existing commercial capabilities could be employed to reduce and monitor infiltration in the WMAs, but that no one technology was appropriate for all seven WMAs. Another conclusion of the forum was that the costs shown in Young, Schroeder, and Carver (1992) were 50% to 80% higher than those reflected by the vendors attending the forum. During the course of the forum a number of U.S. Department of Energy officials and U.S. Department of Energy site subcontractors addressed site-specific constraints that the vendors may not have been taken into account before they submitted their estimated or typical-unit costs.
- In June 2000 the U.S. Department of Energy prepared *Phase I RCRA Facility Investigation/Corrective Measures Study Work Plan for Single-Shell Tank Waste Management Areas* (DOE-RL 2000). Section 4.2 of DOE-RL (2000) identifies a number of general response actions, technology and process options associated with each general response action, and screened each option based on effectiveness, ability to implement, worker safety and cost. While the majority of the processes discussed fell into the ICM category, surface caps, overhead structures and run-on and run-off controls, that are considered interim measures, were identified.

- In April 2001 an engineering report (Anderson 2001) was completed. In addition to evaluating water lines and wells within the WMAs, the report also evaluated surface water both from natural causes and catastrophic events. Alternatives considered in that report include (1) no action, (2) site grading, (3) geo-fabric liners, (4) asphalt concrete paving, (5) building enclosure with asphalt apron, and (6) run-on control. The report recommends that a combination of a building enclosure with asphalt apron and run-on control be implemented. While the building enclosure was not the preferred option (because of the cost) the report concluded that it provided the best operational and technical alternative.

The three potentially viable interim corrective measures selected from among those identified were (1) near-surface barriers, (2) surface barriers, and (3) overhead structures.

F.3.2 NEAR-SURFACE BARRIER

This section describes and evaluates the near-surface barrier option as a near-term ICM, its implementation at WMA S-SX, and costs.

F.3.2.1 Description

The near-surface barrier would consist of an impervious, geo-fabric (geomembrane liner or geosynthetic clay) system over the entire WMA S-SX to direct surface water to the outer boundaries of the tank farm. A run-off collection system consisting of ditches and pipes would be required to route collected surface water to existing drainage routes.

F.3.2.2 Implementation at Waste Management Area S-SX

Implementation of a near-surface barrier would be disruptive to other tank farm activities. The entire area, 18,000 m² (194,000 ft²) at the S tank farm and 20,500 m² (220,000 ft²) at the SX tank farm, would require hand excavation to remove 30 cm (12 in.) of existing soil and subsequent replacement of this soil as a cover over the liner to allow for traffic. The soil would have to be hand excavated because of the tank dome-loading restrictions and the many utilities within the tank farm. Some of these utilities may require support during construction or relocation to a depth below the liner. Installation of the near-surface barrier would require additional time from a typical installation because of the many obstructions protruding above the surface. During the period that the near-surface barrier is required to control surface water, repairs would be required if any tank farm activities required work below the liner.

F.3.2.3 Cost

The estimated costs cited in the engineering report (Anderson 2001) for implementation of a subsurface barrier are \$7.1 million for the S tank farm and \$8.1 million for the SX tank farm.

F.3.2.4 Evaluation Criteria

Tables F.1 and F.2 show decision criteria, weight factors, and score for the near-surface barrier option. For this evaluation, the weight factor was multiplied by one through five to determine the weighted score. A score of one represents little or no impact of the activity to the decision

criterion, and a score of five represents a greatly increased impact of the activity. Note that the weighted factor and decision criteria are the same for all three viable ICMs.

Decision Criteria	Weight Factor	Score	Weighted Score	Highest Possible
Safety	5	4	20	25
Regulatory compliance	3	1	3	15
Life cycle cost analysis	2	2	4	10
Tank integrity	5	3	15	25
Future retrieval and processing	4	2	8	20
Schedule	3	3	9	15
Proven technology	3	1	3	15
Maintainability	3	3	9	15
Operability	2	2	4	10
Constructability	3	4	12	15
	4	3	12	20
Total Weighted Score			99	185

Decision Criteria	Weight Factor	Score	Weighted Score	Highest Possible
Safety	5	4	20	25
Regulatory compliance	3	1	3	15
Life cycle cost analysis	2	2	4	10
Tank integrity	5	3	15	25
Future retrieval and processing	4	2	8	20
Schedule	3	3	9	15
Proven technology	3	1	3	15
Maintainability	3	2	6	15
Operability	2	2	4	10
Constructability	3	3	9	15
Decontamination, decommissioning,	4	3	12	20
Total Weighted Score			93	185

F.3.3 INTERIM SURFACE BARRIER

This section describes and evaluates the interim surface barrier option as a near-term ICM, its implementation at WMA S-SX, and cost.

F.3.3.1 Description

The only surface barrier evaluated is a 6 cm (2.5 in.) layer of asphalt cement pavement. Surface barriers that were not evaluated, but have been used successfully on other projects include various liquid and solid reagents that are applied and allowed to penetrate the surface materials or are mixed with the surface materials to form a crust. A run-off collection system consisting of ditches and pipes would be required to route collected surface water to existing drainage routes.

F.3.3.2 Implementation at Waste Management Area S-SX

Implementation of a surface barrier would be disruptive to other tank farm activities. The entire area, 18,000 m² (194,000 ft²) at the S tank farm and 20,500 m² (220,000 ft²) at the SX tank farm, would require hand excavation to remove 10 cm (4 in.) of existing gravel cover, which would be taken from the site and disposed of if contaminated or used in the production of the asphalt. The material would have to be hand excavated because of the tank dome-loading restrictions and the many utilities within the tank farm. Some of these utilities may require relocation if they are near the surface following removal of the 10 cm (4 in.) of existing materials. Installation of the surface barrier would also take additional time from typical installations to seal the numerous obstructions protruding above the surface.

Adequate compaction of both the subgrade and the asphalt will not be obtained because of the obstructions within the tank farm and the tank dome-loading restrictions. During the period that the surface barrier is required to control surface water, traffic loading may do substantial damage to the surface barrier. The cost to repair the asphalt barrier using the special fine mix could be excessive.

F.3.3.3 Cost

The estimated costs cited in the engineering report (Anderson 2001) for implementation of a surface barrier are \$3.4 million for the S tank farm and \$3.9 million for the SX tank farm.

F.3.3.4 Evaluation Criteria

Tables F.3 and F.4 show decision criteria, weight factors, and score for the interim surface barrier option. For this evaluation, the weight factor was multiplied by one through five to determine the weighted score. A score of one represents little or no impact of the activity to the decision criterion, while a score of five represents a greatly increased impact of the activity. Note that the weighted factor and decision criteria are the same for all three viable ICMs.

Table F.3. S Tank Farm Interim Surface Barrier Evaluation

Decision Criteria	Weight Factor	Score	Weighted Score	Highest Possible
Safety	5	3	15	25
Regulatory compliance	3	1	3	15
Life cycle cost analysis	2	3	6	10
Tank integrity	5	3	15	25
Future retrieval and processing	4	3	12	20
Schedule	3	3	9	15
Proven technology	3	2	6	15
Maintainability	3	4	12	15
Operability	2	2	4	10
Constructability	3	4	12	15
Decontamination, decommissioning, and disposal	4	4	16	20
Total Weighted Score			110	185

Source: Anderson (2001).

Table F.4. SX Tank Farm Interim Surface Barrier Evaluation

Decision Criteria	Weight Factor	Score	Weighted Score	Highest Possible
Safety	5	3	15	25
Regulatory compliance	3	1	3	15
Life cycle cost analysis	2	3	6	10
Tank integrity	5	3	15	25
Future retrieval and processing	4	3	12	20
Schedule	3	3	9	15
Proven technology	3	2	6	15
Maintainability	3	2	6	15
Operability	2	2	4	10
Constructability	3	3	9	15
Decontamination, decommissioning, and disposal	4	4	16	20
Total Weighted Score			101	185

F.3.4 OVERHEAD STRUCTURE

This section describes and evaluates the overhead structure option as a near-term ICM, its implementation at WMA S-SX, and cost.

F.3.4.1 Description

The overhead structure would consist of an enclosed shelter covering the majority of the surface water control area of the WMA. An asphalt apron would be constructed around the perimeter of the structure to capture surface water and route that water to a run-off collection system.

F.3.4.2 Implementation at Waste Management Area S-SX

Erection of the overhead structure would be more complicated than typical erections because of tank dome-loading limitations. This option may require larger-than-normal cranes for erection of the structure and coverings. To span the entire width of the S or SX tank farm (104 m [340 ft] and 107 m [350 ft], respectively) would limit the weight of equipment that could be attached to the structure (e.g., monorails; lighting; heating, ventilation, and air conditioning). Engineers would have to determine if foundations could be constructed in between the tanks at the S and SX farms to decrease the free span distance and to allow greater auxiliary loading of the structures' supports.

The evaluation of which overhead structure to construct must take into account the free span distances of 104 m (340 ft) and 107 m (350 ft). To provide a structure with this free span, a rigid-framed structure may be required. An evaluation should be made of intermediate supports to be located between the tanks. This would allow the structure to be equipped with accessories that may increase productivity of future tank farm operations (e.g., monorail; lighting; and heating, ventilation, and air conditioning). The use of intermediate supports would also allow the use of enclosure systems other than a rigid-framed structure.

The evaluation of overhead structures should also include recently emerging or advanced technologies, (e.g., a domed structure). This technology is purported to provide greater strengths at less cost than conventional structures.

F.3.4.3 Cost

The estimated costs presented in the engineering report (Anderson 2001) for implementation of a building enclosure with an asphalt apron are \$18.3 million for the S tank farm and \$20.8 million for the SX tank farm. Depending on the closure technology used at WMA S-SX, a confinement facility would be required (DOE-RL 2000). If a confinement facility is not required, production would be increased 30% by working within an enclosure (Anderson 2001). Credit was not given to these items in determination of the costs.

F.3.4.4 Evaluation Criteria

Tables F.5 and F.6 show decision criteria, weight factors, and score for the overhead structure option. For this evaluation the weight factor was multiplied by one through five to determine the weighted score. A score of one represents little or no impact of the activity to the decision

criterion, while a score of five represents a greatly increased impact of the activity. Note that the weighted factor and decision criteria are the same for all three viable ICMs.

Table F.5. S Tank Farm Overhead Structure Evaluation

Decision Criteria	Weight Factor	Score	Weighted Score	Highest Possible
Safety	5	2	10	25
Regulatory compliance	3	1	3	15
Life cycle cost analysis	2	5	10	10
Tank integrity	5	2	10	25
Future retrieval and processing	4	1	4	20
Schedule	3	2	6	15
Proven technology	3	1	3	15
Maintainability	3	2	6	15
Operability	2	1	2	10
Constructability	3	2	6	15
Decontamination, decommissioning, and disposal	4	4	16	20
Total Weighted Score			76	185

Source: Anderson (2001).

Table F.6. SX Tank Farm Overhead Structure Evaluation

Decision Criteria	Weight Factor	Score	Weighted Score	Highest Possible
Safety	5	2	10	25
Regulatory compliance	3	1	3	15
Life cycle cost analysis	2	5	10	10
Tank integrity	5	2	10	25
Future retrieval and processing	4	1	4	20
Schedule	3	2	6	15
Proven technology	3	1	3	15
Maintainability	3	2	6	15
Operability	2	1	2	10
Constructability	3	2	6	15
Decontamination, decommissioning, and disposal	4	4	16	20
Total Weighted Score			76	185

Note: No credit was given for an estimated 30% productivity improvement for tank farm activities following structure construction or that closure activities may require an enclosure.

Source: Anderson (2001).

F.3.5 NEAR-TERM INTERIM CORRECTIVE MEASURES SUMMARY

This section summarizes the evaluation of the three potential near-term ICMs (near-surface barriers, surface barriers, overhead structures) and provides a comparison of the evaluation criteria and conclusions based on the evaluation. The near-surface barrier, surface barrier, and overhead structures options evaluated presented problems for implementation. Implementation of the near-surface and surface barriers would require extensive hand labor because of tank dome-loading restrictions and numerous obstructions protruding to the surface. Implementation of the overhead structures would require free span distances that may stretch the limits of current technologies involved in construction or would require foundations to be constructed in the area between tanks.

Table F.7 summarizes the estimated costs for each option by tank farm.

Table F.7. Interim Corrective Measures Cost Summary

Option	S Tank Farm Estimated Costs	SX Tank Farm Estimated Costs
Near-surface barriers	\$7,058,000	\$8,123,000
Surface barriers	\$3,373,000	\$3,892,000

Table F.8 summarizes the evaluation criteria and weighted scores for the options evaluated for minimizing infiltration at the S and SX tank farms.

Table F.8. Interim Corrective Measures Evaluation Summary

Decision Criteria	Weighted Score S Tank Farm			Weighted Score SX Tank Farm		
	Subsurface Barrier	Surface Barrier	Overhead Structure	Subsurface Barrier	Surface Barrier	Overhead Structure
Safety	20	15	10	20	15	10
Regulatory compliance	3	3	3	3	3	3
Life cycle cost analysis	4	6	10	4	6	10
Tank integrity	15	15	10	15	15	10
Future retrieval and processing	8	12	4	8	12	4
Schedule	9	9	6	9	9	6
Proven technology	3	6	3	3	6	3
Maintainability	9	12	6	6	6	6
Operability	4	4	2	4	4	2
Constructability	12	12	6	9	9	6
Decontamination, decommissioning, and disposal	12	16	16	12	16	16
Total Weighted Score	99	110	76	93	101	76

Any of the three potential near-term ICMs could be implemented to reduce infiltration at WMA S-SX. The cost versus benefits (i.e., reduction in contaminant concentrations in the groundwater) of implementing any of the interim measures should be considered because sufficient time may have elapsed between when the leaks occurred and the present to effectively reduce the contaminant concentrations in the groundwater. Additionally implementing ICMs may divert funding from other tank waste remediation activities such as waste retrieval.

The evaluation of options in Anderson (2001) resulted in a recommendation to implement the overhead structure. This recommendation is based on the *summary* of the evaluation criteria that ranked the overhead structure lowest for both S and SX tank farms. The weighted scores presented are subjective and represent a best-estimate effort to account for the relative importance of the different evaluation criteria presented. The estimated cost for the overhead structure is considerably higher than the other options evaluated and this variation is not well captured in the weighted ranking. Anderson (2001) did not provide credit for an estimated 30% productivity gain for tank farm operations within the enclosure or that enclosure would be required for certain tank farm closure alternatives.

F.3.6 ADDITIONAL POTENTIAL INTERIM CORRECTIVE MEASURES

This section identifies additional potential ICMs for consideration at WMA S-SX. These ICMs generally involve a greater commitment of resources than the ICMs discussed in Section F.3.5 and require a more thorough site-specific evaluation prior to selecting an ICM for implementation at WMA S-SX. Any evaluation of ICMs must include consideration of continued storage of waste in the tanks and future plans to retrieve waste from the tanks as well as cost versus benefits of the technologies in terms of reducing groundwater impacts. If warranted, detailed evaluation of ICMs for WMA S-SX would be conducted in a corrective measures study.

F.3.6.1 Interim Corrective Measure Technologies for Soil Contamination

This section describes the ICM technologies for soil contamination that are described in the Phase 1 RFI/CMS work plan (DOE-RL 2000) and in *Feasibility Study of Tank Leakage Mitigation Using Subsurface Barriers* (Treat et al. 1995).

F.3.6.1.1 Containment Technologies. Containment technologies use physical measures to isolate and reduce the horizontal and vertical movement of contaminants.

Grout Walls. Grout walls are formed by either injecting grout under pressure directly into the soil matrix (permeation grouting) or in conjunction with drilling (jet grouting) at regularly spaced intervals to form a continuous low-permeability barrier. Grout walls could be installed either vertically or directionally in an effort to create a barrier underneath the contaminant plume in the soil (DOE-RL 2000). A large number of boreholes would be required to construct a barrier. A grout containment barrier was previously evaluated for the AX tank farm as a means to contain potential retrieval leakage (Norman 1999). In the AX tank farm study, grout injection borings were directionally drilled beneath the tanks on approximately 1.5 m (5 ft) centers. Installation of a horizontal grout blanket beneath the four tanks in the AX tank farm **was** estimated to cost approximately \$200 million. One of the issues identified with this technology

was the difficulty in verifying the integrity of the grout barrier. Grout walls are potentially applicable at WMA S-SX, however, the contamination has reached the groundwater and the ability to implement this technology and determine its effectiveness are of concern and would require further evaluation.

Cryogenic Barrier. Cryogenic (or freeze-wall) barriers are formed by recirculating chilled brine or other refrigerants through an array of closely spaced wells or freeze pipes. As the soil surrounding and between these wells or freeze pipes cools and freezes, the water in the voids freezes and expands. The freezing and expanding water effectively creates an impermeable barrier. Cryogenic barriers may be applicable at WMA S-SX although it is unclear if the technology would perform as planned if it were necessary to inject supplemental water into the highly transmissive soils of the Hanford Site. In addition, maintenance of a cryogenic barrier requires a long-term commitment of resources. Contamination has reached the groundwater, and the ability to implement this technology and determine its effectiveness is of concern and would require further evaluation.

Dynamic Compaction. Dynamic compaction is used to densify the soil; compact buried solid waste; and reduce the void spaces in the soil, which can reduce the hydraulic conductivity of the soil and the mobility of contaminants. This process is accomplished by dropping a heavy weight onto the ground surface. This technology is commonly used in coordination with caps; it would have limited application in the tank farm area because of the graveled surface and the potential tank dome-loading during the compaction process.

Circulating Air Barriers. The circulating air barrier technology would create a dry zone under the area of confinement through which no liquids could penetrate until a critical liquid saturation was exceeded. For most sediments at the Hanford Site, critical saturation is on the order of 5% to 25%. The water under the tanks is essentially immobile and, if kept at or below the critical saturation value, would remain immobile. Circulating air barrier technology injects dry air from an array of either vertical or horizontal wells. The air is forced through porous soils to extraction wells, vaporizing water in the process. Circulating air barrier technology is applicable at WMA S-SX although no large-scale field tests have been performed.

Radio Frequency Desiccating Subsurface Barriers. A radio frequency heating process can be used for the formation of an active desiccating barrier underneath underground storage tanks. Electrodes are installed in the soil between the source of the contamination and groundwater using horizontal drilling techniques. The radio frequency energy applied to the electrodes heats a 2 to 3 m (6 to 10 ft) thick layer of soil to temperatures above 100°C (212 °F) to evaporate the moisture. Electrodes are perforated and maintained under vacuum to remove the steam and volatile organics for aboveground treatment and disposal. Radio frequency desiccating subsurface barriers may be applicable at WMA S-SX although the concept has not been tested at the Hanford Site.

Close-Coupled Injected Chemical Barriers. Unlike the concept of subsurface barriers installed at some depth below the tanks or below a containment plume as discussed previously for grout walls and cryogenic barriers, close-coupled injected chemical barriers are formed against the sides and bottom of an individual underground storage tank. It is unlikely that the close-coupled chemical barrier concept would be applicable at WMA S-SX because of the

problems of induced stresses on the tanks and the inability of installing a conical jet grout shell given the confining limitations among the Hanford Site underground storage tanks. In addition, the concept has not been tested outside of the laboratory.

Induced Liquefaction Barriers. Induced liquefaction is a close-coupled subsurface barrier option that combines the concepts of sheet metal piling to create a vertical barrier with caisson-drilled horizontal jet grouting. Although this technology may be applicable at WMA S-SX, no full-scale application of this technology for waste management or environmental restoration purposes is known.

F.3.6.1.2 Removal Technologies. Removal technologies include the excavation of contaminated soils or buried solid waste. After removal, the soil **and** debris may require ex situ treatment to meet disposal requirements or to reduce waste volume. Removal technologies could be considered for localized areas in the tank farms where leaks occurred from piping or diversion boxes at near-surface to mid-depth. Removal would not likely be effective for capturing the mobile contaminants because of the relatively high recharge rate in the tank farms and the elapsed time since the leaks occurred.

F.3.6.1.3 In Situ Treatment Technologies. In situ treatment technologies are oriented at treating the contamination in place to either extract the contaminants of concern or to stabilize and isolate contaminated soil to prevent migration to the groundwater.

Electrokinetic Separation. Electrokinetic separation can be used for organics, inorganics, and radioactive contaminants. This technology involves applying an electrical potential across the contaminated zone by using electrodes placed in the ground. Remediation by electrokinetics is based on the migration of water and ions in an electrical field. The application of electrokinetic separation at the tank farms may be limited since water is required to move ions between electrodes. Application in unsaturated soils may require water addition that could cause unwanted migration of contaminants.

In Situ Biodegradation. In situ biodegradation relies on microbial transformation of organic contaminants. Biodegradation is effective on organic contaminants but is not effective on radionuclides or inorganics. Therefore, this technology would have limited application in the tank farm area.

Solidification. Solidification can be used for organics, inorganics, and radiological contaminants. This process involves drilling holes to the desired depth, then injecting the solidification and stabilization agents into the soil with high-pressure pumps. Variations of solidification include jet injection and shallow-soil mixing. Jet injection involves drilling a small-diameter hole using a downward jet of air or water then pumping the solidification agent out laterally through jets located near the bottom of the drill pipe. Shallow-soil mixing is performed using a crane-mounted auger head to mix the soil and solidification agent. Solidification methods are potentially applicable at WMA S-SX. Access to contaminants beneath the **tanks** would be difficult and would require directional drilling or angle drilling. Solidification requires an understanding of the location and distribution of contaminants. Stabilization of large plumes extending from the base of the tank to the groundwater would

require a substantial commitment of time and resources. Solidification technologies would serve to delay the migration of contaminants to the groundwater.

Grout Injection. Grout is injected into the soil matrix, encapsulating the contaminants. The injection process produces a monolithic block that can be left in place or excavated for disposal elsewhere. Although grout injection is applicable at WMA S-SX, if the encapsulated contaminants are left in place future use of the site may be limited. Grouting contaminated soils deep in the vadose zone beneath the tanks would be an issue.

Deep Soil Mixing. Deep soil mixing is performed using large augers and injector-head systems to inject and mix solidifying agents into contaminated soil. Although deep soil mixing is applicable at WMA S-SX, if the encapsulated contaminants are left in place future use of the site may be limited. Using this technology to mix contaminated soil deep in the vadose zone directly beneath or adjacent to the tanks would be problematic.

Vitrification. Vitrification can be used for organics, heavy metals, and radionuclides. In situ vitrification involves the application of an electrical current to the soil to bring it to a temperature sufficient to melt the soil (1400 to 2000 °C [2552 to 3632 °F]). The process forms a stable, vitrified mass when cooled, chemically incorporates most inorganics including heavy metals and radionuclides, and destroys or removes all organic contaminants. In situ vitrification is probably not applicable at WMA S-SX because process depths are limited and the technology ~~has~~ very limited (extremely unlikely) potential for use in tank farms or near tanks that are storing waste.

Soil Flushing. Soil flushing can be used for organics, inorganics, and radioactive contaminants. In situ soil flushing involves the extraction of contaminants from the soil by injecting ~~an~~ extractant or elute (e.g., water or some other suitable solvent) through the contaminated soils. The extraction fluids solubilize or elute the contaminant from the soil. The resultant solution must be recovered through extraction wells and treated at the surface by a treatment system (e.g., ion-exchange system). Soil flushing is potentially applicable at WMA S-SX.

Soil Vapor Extraction. The soil vapor extraction process induces airflow through the soil matrix with an applied vacuum that facilitates the mass transfer of adsorbed, dissolved, or free phases of the contaminant to the vapor phase. Because soil vapor extraction is best used for volatile organic compounds and fuels, it would have limited application in the tank farm area.

Monitored Natural Attenuation. Monitored natural attenuation relies on natural processes to lower contaminant concentrations through physical, chemical, or other biological processes that, “under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants” (EPA 1999) until cleanup levels are met. Although natural attenuation methods may be readily implemented, significant action or commitment of resources (e.g., personnel to conduct sampling and perform analytical work, construction activity, and loss of land use) may be required.

F.3.6.1.4 Ex Situ Treatment Technologies. Ex situ technologies would be used in conjunction with removal technologies ~~as~~ discussed in Section F.3.6.1.2. Ex situ treatment technologies would have potential application for near-surface spills and leaks but would not have application for tank leaks near tanks used for storage of high-level waste. Ex situ treatment of contaminated

soils would likely require excavation by hand to remove contaminated soils within the *tank* farms. Worker exposures associated with hand excavation of soils contaminated from concentrated tank or transfer line leakage would be prohibitive. Additionally, an enclosure structure would also likely be required to reduce the potential for airborne contamination during excavation. Remote removal techniques are possible but would require research and development prior to being considered for deployment in the tank farms.

Biodegradation. Ex situ biodegradation is essentially the same as in situ biodegradation, except that the soil is excavated and placed in a system or pile where treatment is applied (DOE-RL 2000). Biodegradation is effective on organic contaminants, but is not effective on radionuclides or inorganics. Therefore, this technology would have limited application in the tank farm area.

Soil Washing. Soil washing is a process that applies to coarse-grained soils contaminated with a wide variety of metal, radionuclide, and organic contaminants. This process uses a wash solution (e.g., water) to remove soil contaminants by dissolving or suspending the contaminants in solution or concentrating them through particle size separation, gravity separation, and attrition scrubbing. The wash solution requires treatment to remove the contaminants that have been washed and desorbed from the soil. Although soil washing could be applicable at WMA S-SX, there are significant safety and contamination control issues associated with excavation of the more contaminated soils beneath the tanks, particularly while the tanks are still storing waste.

Solidification and Stabilization. Solidification and stabilization uses admixtures to encapsulate excavated soil and render inert various hazardous substances. This process is targeted at metals, radionuclides, and other organics. Stabilizing agents include cement, asphalt, and polymeric materials. Solidification and stabilization is applicable at WMA S-SX.

Thermal Desorption. Thermal desorption uses relatively low-temperature heat (150 to 425 °C [302 to 842 °F]) to volatilize organic contaminants from soil. A carrier gas or vacuum is used to collect and transport the volatilized organics to a gas-treatment system. Thermal desorption is only effective on organics, and it would have limited applicability at WMA S-SX.

Encapsulation. Encapsulation is accomplished by fixing individual particles in a solid matrix as discussed in "Solidification and Stabilization" or by enclosing a quantity of waste in an inert jacket or container. Encapsulation of contaminated soils is potentially applicable at WMA S-SX excluding the issues associated with excavation of the contaminated soils.

F.3.6.2 Interim Corrective Measure Technologies for Groundwater Contamination

This section describes the ICMs for groundwater contamination that are defined in the Phase 1 RFI/CMS work plan (DOE-RL 2000) and in *Feasibility Study of Tank Leakage Mitigation Using Subsurface Barriers* (Treat et al. 1995).

F.3.6.2.1 Hydraulic Containment: Extraction Wells. Hydraulic containment involves placement of extraction wells close along a line or surrounding an area, and pumping the groundwater to form depression zones, thereby creating a barrier to the passage of groundwater

and contaminants contained in the groundwater. The extracted groundwater may require treatment to remove the contaminants.

Hydraulic containment using extraction wells is applicable at WMA S-SX. However, this may not make sense within the context of other waste sites in the 200 Areas, and the potential exists for extracting contamination from nearby cribs and environmental restoration disposal sites.

F.3.6.2.2 Impermeable Barriers. Impermeable barriers are solid walls that are placed into the subsurface to retard the movement of groundwater. Groundwater flowing toward a barrier will divert away from and eventually flow around the barrier. A barrier could be supplemented with extraction wells at the ends of the barrier to prevent mobile contaminants from migrating around the barrier.

Sheet-Pile Barrier. Sheet-pile barriers are constructed by driving interlocking sheet-piles into the ground with either vibratory or impact pile drivers. This barrier would need to be coupled with a horizontal barrier to form a complete barrier envelope. Sheet-pile barriers were tested in the 100-N Area of the Hanford Site and were unsuccessful. The piling was destroyed after penetrating to a depth of 9.2 m (30 ft). Based on the depth to groundwater, installation of a sheet-pile barrier at WMA S-SX would not be possible.

Cryogenic (Freeze-Wall) Barrier. A cryogenic or freeze-wall barrier is formed using two methods. A closed-loop system recirculates chilled brine or other refrigerants through an array of closely spaced wells or pipes, freezing and expanding the water in the soil voids surrounding the freeze pipes. An open loop system involves the injection of liquid nitrogen into the ground through perforated well casings. Cryogenic barriers may be applicable at WMA S-SX. Maintenance of a cryogenic barrier requires a long-term commitment of resources.

Chemical Jet Grout Encapsulation. Chemical jet grout encapsulation uses primarily high-pressure jet grouting to form columns of grouted soil via directionally drilled wells. Standard grouts such as portland cements or bentonite clays are used. More exotic grouts could be used for enhanced set times and better compatibility with Hanford soils. Chemical jet grout encapsulation is applicable at WMA S-SX.

Jet Grout Curtains. Jet grout curtain placement is similar to grout encapsulation described above, except that both vertical and horizontal wells, rather than directionally drilled wells, are used for injection. Jet grout curtain technology is applicable to WMA S-SX.

Permeation Chemical Grouting. Permeation chemical grouting is similar to jet grouting except that lower pressures are used for injection. Permeation chemical **grouts** could be injected using both vertical and horizontal wells. Permeation chemical grouting is applicable at WMA S-SX, although performance is highly dependent upon the properties of the grouting material used and the properties of the soil.

Wax Emulsion Permeation Grouting. A mineral wax-bentonite emulsion, called 'Montan' wax, has been developed for grouting applications. Montan wax grout consists of a stable emulsion of Montan wax, water, and a surfactant. Once inside the soil matrix, the wax particles begin to aggregate and move through void spaces until they bridge an opening and become fixed. Bridging the openings between pores reduces the permeability of the soil. Wax emulsion

permeation tests have been conducted at the Hanford Site and have shown that soil hydraulic conductivity can be reduced by two to three orders of magnitude.

Silica, Silicate Permeation Grouting. Sodium silicate permeation grouting uses a silicate-based chemical grout with favorable characteristics that can be controlled by altering the formulation of the grout. By altering the proportions of the components of sodium silicate grout, the set time and grout viscosity can be controlled. Colloidal silica is also being explored for use in forming subsurface barriers at the Hanford Site. Colloidal silica is a colloidal suspension with gelling properties. Tests using Hanford soils have been performed on sodium silicate grouts and colloidal silica, and have shown that soil hydraulic conductivity can be reduced by three to four orders of magnitude. This technology is potentially applicable at WMA S-SX.

Polymer Permeation Grouting. Polymer permeation grouting employs an injected liquid monomer or resin that converts to a polymer (in place) to form a concrete-like monolithic barrier. Polymer-forming chemicals could be injected into the ground using the same methods for emplacing cement slurry walls. Although some polymer grouts (e.g., furfuryl alcohol) are chemically incompatible with Hanford Site soils, polymer permeation grouting is applicable at WMA S-SX.

Formed-in-Place Horizontal Grout Barriers. Placement of formed-in-place horizontal grout barriers involves the use of a proprietary technology to generate a barrier slab of uniform thickness between guide wires placed by horizontal drilling methods. The technology uses high-pressure jets mounted on a reciprocation machine tool. The grout slurry sprayed through the jets disrupts and mixes soils to a mortar-like consistency between the guide pipes. The machine tool passes through this semi-liquid material as the hardware is pulled along the guide wires, forming a uniform barrier behind it. Adjacent panels would be placed at the edge of the previous panel (before it hardens totally), overlapping the previous panel to some extent to form an extended slab. Formed-in-place horizontal grout barriers may be applicable at WMA S-SX although the technology has never been incorporated at full scale.

Concepts Not Considered Feasible for the Hanford Site. The following concepts are not considered feasible for Hanford Site underground storage tank applications and are listed here for completeness only:

- Soil fracturing
- Longwall mining
- Modified sulfur cement
- Sequestering agents
- Reactive barriers
- Impermeable coatings
- Microtunneling
- In situ vitrification barriers
- Soil saw
- Deep soil mixing
- Slurry walls
- Soil-mixed walls.

F.3.6.2.3 **In Situ Treatment Technologies.** In situ treatment technologies are oriented at treating the contamination in place to either selectively extract contaminants or to stabilize and isolate contaminants from migrating in the groundwater.

Adsorption-Type Treatment Barrier. Permeable treatment beds and barriers are constructed by excavating a trench and backfilling it with a mixture of soil and adsorbents. The bed is placed downgradient of the contaminated plume. As the natural groundwater flow carries the contaminants through the bed, the contaminants that the barrier is designed to remove are adsorbed onto the bed. Adsorption-type treatment barriers would have limited applicability to WMA S-SX due to the depth of soil that would have to be excavated to reach groundwater.

Phosphate Precipitation Barrier. Phosphate compounds are used in these barriers to precipitate heavy metals (e.g., strontium-90) in the soil matrix. This technology is in the developmental stages and its applicability to WMA S-SX is not known.

Soil Flushing. Soil flushing is described in Section F.3.6.1.3. This technology is considered innovative and was considered for remediating a deep (21.4 m [70.2 ft]) aquifer (DOE-RL 1997). Use of the soil flushing technology requires mounding of the water table over a relatively large area.

Monitored Natural Attenuation. Monitored natural attenuation relies on natural processes to lower contaminant concentrations through physical, chemical, and other biological processes that, "under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants" (EPA 1999) until cleanup levels are met. Although natural attenuation methods may be readily implemented, significant action or commitment of resources (e.g., personnel to conduct sampling and perform analytical work, construction activity, and loss of land use) may be required. Monitored natural attenuation would have limited applicability at WMA S-SX for the long-lived mobile radionuclides.

F.3.6.2.4 **Ex Situ Treatment Technologies.** Ex situ treatment technologies are used to remove contaminants from groundwater after the groundwater has been pumped to the surface. Ex situ treatment technologies that are potentially applicable at WMA S-SX are noted below.

Precipitation Technology. Precipitation technology is used to remove metals and radionuclides from water by precipitation.

Membrane Technology. Membranes can be considered for the treatment of radionuclides (e.g., strontium-90). The membrane adsorbs the contaminant. This technology is in the developmental stage.

Ion-exchange Technology. Ion-exchange technology removes ions from solution by adsorption on a solid medium, typically an ion-exchange resin bed or column. As the groundwater is passed through the resin, ionic species in the groundwater exchange with ions on the resin and are adsorbed onto the surface of the resin.

Wet Air Oxidation. Wet air oxidation is based on a liquid-phase reaction between organics in the wastewater and compressed air. This process is used for the treatment of organics and may have limited applicability at WMA S-SX.

Activated Carbon. When contaminated wastewater is passed over activated carbon beds, organic hydrocarbon contaminants are absorbed onto the carbon. This process is used for the treatment of organics and may have limited applicability at WMA S-SX.

Tritium Treatment Technologies. The most successful treatment systems for tritium treatment and separation are gaseous phase applications as used in commercial nuclear power operations. Technologies being considered or being used for tritium are a combination of electrolysis and catalytic exchange, bithermal catalytic exchange, and membrane separation.

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APPENDIX G

REGULATORY ANALYSIS

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LIST OF TERMS

ILCR	incremental lifetime cancer risk
RCRA	<i>Resource Conservation and Recovery Act of 1976</i>
WMA	waste management area

G.1.0 INTRODUCTION

Phase I RCRA Facility Investigation/Corrective Measures Study Work Plan for Single-Shell Tank Waste Management Areas (DOE-RL 2000) provides the regulatory framework for the ***Resource Conservation and Recovery Act of 1976*** (RCRA) Corrective Action Program.

This regulatory framework is based on federal statutes and regulations, Washington State statutes and regulations, the ***Hanford Federal Facility Agreement and Consent Order*** (HFFACO; Ecology et al. 1989); and the Hanford Site RCRA Permit (Ecology 2001). Applicable or relevant and appropriate requirements are provided in Appendix F of DOE-RL (2000).

The purpose of a field investigation report is to summarize data from a waste management area (WMA) investigation and evaluate the data to the extent necessary to determine the need for immediate action through interim measures or accelerated interim corrective measures at the WMA. At a minimum, the data is evaluated to determine the potential risk associated with hypothetical exposure to soil and groundwater at the WMA boundary as described in Section 4.0 of DOE-RL (2000). If the potential near-term risk to human health is excessive, the U.S. Department of Energy and Washington State Department of Ecology may propose one or more interim measures to mitigate the risk or may initiate an accelerated corrective measure study to evaluate and compare more complex interim corrective measures.

The evaluation of the risks associated with existing contamination serves several purposes. Some of these purposes include the following:

- Establish the need for additional interim measures or interim corrective measures
- Provide necessary input to Hanford Site-wide cumulative risk assessments
- Serve as a basis to begin identifying cleanup standards for closure.

Cleanup standards are based on both regulatory requirements and the potential risk to human health and the environment. The potential risk depends in part on the hypothetical exposure scenario, which in turn depends on the assumed land use (including surface water and groundwater). Exposure and land use scenarios are also important in identifying the appropriate regulatory requirements for cleanup. For example, the determination of cleanup standards under the “The Model Toxics Control Act Cleanup Regulation” (WAC 173-340) depends on whether an unrestricted (residential) or industrial scenario is applied, and the use of alternate concentration limits under “Concentration Limits” (WAC 173-303-645(5)) depends in part on future groundwater uses. In 1999, the U.S. Department of Energy issued ***Final Hanford Comprehensive Land-Use Plan Environmental Impact Statement*** (DOE 1999), which used the ***National Environmental Policy Act of 1969*** process to evaluate several land uses for the Hanford Site planned over the next 50 years. That environmental impact statement and associated record of decision “Hanford Comprehensive Land-Use Plan Environmental Impact Statement (HCP EIS), Hanford Site, Richland, Washington; Record of Decision (ROD)” (64 FR 61615), identify ‘industrial-exclusive use’ as the planned use for the 200 Areas Central Plateau, an area that encompasses the 200 East and 200 West Areas. The Washington State Department of Ecology is evaluating how the U.S. Department of Energy land-use planning efforts fit within the Washington State Department of Ecology cleanup framework; the agency has not agreed at this time to an industrial use scenario. Therefore, potential risk and the regulatory requirements for establishing media cleanup standards for the RCRA Corrective Action Program cannot be

finalized. Appendix E of this report presents the **risk** assessment and evaluation approach and results that considers several potential exposure scenarios identified in DOE-RL (2000).

G.2.0 REGULATORY PERFORMANCE MEASURES

Table G. 1 identifies quantitative performance measures for various constituents, including hazardous and radiological contaminants. The level of protection established by the standards is expressed in terms of the maximum dose or contaminant concentration under various exposure scenarios. Each standard, therefore, reflects the determination by the regulatory agency of an appropriate level of protection that should be provided to protect human health. Generally, the spectrum of regulations reflected in Table G. 1 demonstrates that the level of protection provided by regulatory agencies is consistent among the regulations whether they apply to dangerous contaminants (e.g., chemicals and metals) or radiological contaminants. The level of protection provided under the regulations ranges from between 1 incremental lifetime cancer **risk** (ILCR) in 10,000 (1.0×10^{-4}) and 1 in 1,000,000 (1.0×10^{-6}) on an annual basis.

The most important regulations related to this WMA S-SX field investigation report are those addressing cleanup of soils and groundwater and the associated risk or dose to human health through the groundwater exposure pathway. The following sections discuss compliance with the applicable regulations.

Table G.1. Regulatory Performance Measures

Regulation	Requirement	Performance Measure	Point-of-Comoliance	Notes
DOE Order 5400.5				
Protection of the Public	All pathways for LLW except air (mrem/yr)	25	100 m downgradient for groundwater, at waste site for diect exposure	100 years of institutional control.
	All pathways including other Hanford sources per 10 CFR 20, DOE Order 5400.5 and DNFSB 94-2 (mrem/yr)	100	100 m downgradient for groundwater, at waste site for direct exposure	--
Protection of Groundwater (40 CFR 141)	Beta/proton emitters (mrem/yr)	4	100 m downgradient	100 years of institutional control. 500 years of passive control. 10,000 years for impacts analysis. Assumes water ingestion of 2 L/day. Alpha emitters: 15 pCi/L = 40 mrem/yr radon: 3 pCi/L = 20 mrem/yr
	Alpha emitters (pCi/L)	15		--
40 CFR 141 and DOE Order 5400.5	Drinking water standards for select constituents with the potential for release to groundwater during ooperations. retrieval actions. or postclosure			
MCLs and derived concentration guide for select constituents Source: 40 CFR 141	H-3	20,000 pCi/L	Drinking water source	1,000 yr for compliance analysis. Alpha Emitters: 15 pCi/L = 40 mrem/yr.
	C-14	2,000 pCi/L		
	I-129	1 pCi/L		
	U	0.02 mg/L (Total)		
	Tc-99	900 pCi/L		
	Cs-137	200 pCi/L		
Cr	0.5 mg/L			

LLW = low-level waste.

MCL = maximum contaminant level.

G.3.0 REGULATORY COMPLIANCE FROM FIELD DATA

Regulatory compliance data for soils and groundwater collected during the field investigation activities are presented with comparison to regulatory requirements in Appendices B and C. The following sections discuss the new WAC 173-340 revision related to assessing derived soil concentrations for groundwater protection, “Deriving Soil Concentrations for Ground Water Protection” (WAC 173-340-747), and groundwater contamination present in WMA S-SX groundwater monitoring.

G.3.1 SOIL DATA

Under WAC 173-340-747 the term ‘soil concentration’ means the concentration in the soil that will not cause an exceedance of the groundwater cleanup level established under “Ground Water Cleanup Standards” (WAC 173-340-720). Six different methodologies can be used to determine if the criterion has been met. This WMA S-SX field investigation report uses the alternative fate and transport model (WAC 173-340-747(8)). The values used in the fate and transport modeling are based on best estimates and do not comply with the default values in WAC 173-340-747. The values used provide an estimate of groundwater impacts from the soil inventory estimate (see report main text Sections 3.3 and 4.2 and also Appendix E). Numerical simulation results are obtained on long-term transient contaminant concentrations at the water table and for compliance at the WMA boundary, 200 West fence boundary, 200 Area exclusion boundary, and the shoreline at the Columbia River. These compliance points are based on DOE-RL (2000). However, since the 200 Area and exclusion boundaries are relatively close, the 200 Area boundary is replaced by the 200 West fence boundary. For vadose zone modeling, three representative (west-east) cross-sectional models for the S and SX tank farms were considered:

- Cross-section through tanks, S-106, S-105, and S-104 (S-CC’)
- Cross-section through tanks SX-109, SX-108, and SX-107 (SX-DD’)
- Cross-section through tanks SX-115, SX-114, and SX-113 (SX-FF’).

Table G.2 provides the case numbers and descriptions for the numerical simulations as discussed in Section 4.0 of the main text and Appendix E. Numerical results are obtained on long-term transient contaminant concentrations and at compliance boundaries for each cross-section at WMA S-SX (i.e., cross-sections S-CC’, SX-DD’ and SX-FF’); 200 West fence; 200 Area exclusion boundary; and the Columbia River shoreline (DOE-RL 2000).

The groundwater concentration values based on inventory show that for the three cross-sections analyzed (i.e., S-CC’, SX-DD’, and SX-FF’), drinking water standards (40 CFR 141) will be exceeded. Tables G.3 and G.4 list the predicted technetium-99, chromium, and nitrate levels and the associated 40 CFR 141 limits. Table G.3 lists the groundwater concentration values for three cross-sections at the WMA S-SX boundary. Table G.4 lists the groundwater concentration values for the 200 West fence, 200 Area exclusion boundary, and the Columbia River shoreline.

Table 6.2. Case Descriptions for the Two-Dimensional Simulations

Case No.	Description*	Interim Barrier	Inventory Distribution	Meteoric Recharge (mm/yr)
1	Base case (no action alternative)	No	Uniform	100
2	Barrier alternative	Yes	Uniform	100
3	Water-line leak (25,000 gal)	No	Uniform	100
4	Clastic dike	No	Uniform	100
5	Nonuniform inventory	No	Nonuniform	100
6	Nonuniform inventory with barrier	Yes	Nonuniform	100
7	Displaced nonuniform barrier	No	Displaced	100
8	Density and viscosity effects	No	Uniform	100
9	Base case with 50% recharge	No	Uniform	50
10	Base case with 30% recharge	No	Uniform	30
11	Base case with 10% recharge	No	Uniform	10
13	Water-line leak (200,000 gal)	No	Uniform	100

Table G.3. Modeled Groundwater Concentrations (Average Weighted) at the Waste Management Area S-SX Boundary

Cases	Waste Management Area S-SX Boundary									
	S-CC*			SX-DD*			SX-FF*			
	Technetium-99 (pCi/L)	Chromium (µg/L)	Nitrate (µg/L)	Technetium-99 (pCi/L)	Chromium (µg/L)	Nitrate (µg/L)	Technetium-99 (pCi/L)	Chromium (µg/L)	Nitrate (µg/L)	
Case 1	108,303	2,213	664,506	968,367	81,051	1,013,000	225,324	3,564	795,585	
Case 2	72,309	406	450,727	144,430	7,558	684,500	158,646	677	537,589	
Case 3	NA	NA	NA	NA	NA	1,018,000	224,774	3,585	799,512	
Case 4	NA	NA	NA	963,655	80,265	NA	NA	NA	NA	
Case 5	1,397,182	30,410	6,216,243	4,263,016	352,241	4,382,000	2,063,180	28,391	3,441,513	
Case 6	970,724	5,189	4,435,798	680,842	37,588	3,339,000	1,570,750	6,073	2,622,367	
Case 7	4,519,048	52,149	19,218,126	9,102,496	599,477	13,100,000	5,721,457	50,044	10,288,413	
Case 8	109,403	2,214	670,553	989,573	82,621	1,024,000	228,151	3,570	804,224	
Case 9	72,522	704	446,721	294,044	17,443	713,500	156,133	1,297	560,365	
Case 10	40,989	237	256,661	87,491	5,692	432,400	96,837	464	339,596	
Case 11	8,301	126	53,555	53,209	3,265	98,950	21,857	246	77,713	
Case 12	105,711	2,090	470,283	459,994	34,973	513,700	245,979	3,007	403,447	
Case 13	NA	NA	NA	NA	NA	952,200	192,024	3,395	747,834	
Regulatory Standard	900 pCi/L	50 µg/L	45,000 µg/L	900 pCi/L	50 µg/L	45,000 µg/L	900 pCi/L	50 µg/L	45,000 µg/L	

*Groundwater concentrations given are the breakthrough values for the cross-sections. See Appendix E.

Table G.4. Modeled Groundwater Concentrations (Average Weighted) at Specified Compliance Points

Cases	200 West Area Fence			200 Area Exclusion Boundary			Columbia River Shoreline		
	Technetium-99 (pCi/L)	Chromium (µg/L)	Nitrate (µg/L)	Technetium-99 (pCi/L)	Chromium (µg/L)	Nitrate (µg/L)	Technetium-99 (pCi/L)	Chromium (µg/L)	Nitrate (µg/L)
Case 1	4,890	449	9,490	380	34.9	737	128	11.9	249
Case 2	1,910	85.5	4,310	147	6.44	334	51.1	2.31	115
Case 3	4,890	452	9,500	379	35.1	738	129	12.0	250
Case 4	4,890	447	9,460	379	34.8	735	128	11.8	249
Case 5	5,290	523	10,200	411	40.8	796	139	13.8	269
Case 6	2,090	103	4,800	162	7.76	373	56.1	2.77	129
Case 7	6,890	778	13,100	542	60.9	1,030	178	20.2	339
Case 8	4,960	455	9,610	385	35.4	747	130	12.0	252
Case 9	2,500	154	5,320	191	11.7	409	66.7	4.14	142
Case 10	1,320	55.5	3,040	99.7	4.11	231	35.4	1.50	81.7
Case 11	308	7.27	745	22.6	0.513	54.8	8.28	0.189	20.1
Case 12	4,950	451	9,630	384	35.1	748	130	11.9	253
Case 13	4,760	455	9,420	368	35.3	730	125	12.0	248
Regulatory Standard	900 pCi/L	50 µg/L	45,000 µg/L	900 pCi/L	50 µg/L	45,000 µg/L	900 pCi/L	50 µg/L	45,000 µg/L

The predicted groundwater concentrations exceed the regulatory standards at the WMA and for most of the cases at the 200 West fence boundary. Exceedances of the groundwater maximum contaminant levels occur for all three modeled constituents at the WMA S-SX boundary (Table G.3). At the 200 West Area fence, nitrate and chromium for Case 11 did not exceed the groundwater maximum contaminant levels (Table G.4). At the 200 Area exclusion boundary (i.e., the rest of the Central Plateau including 200 Area North extending north to the base of Gable Butte), nitrate and technetium-99 did not exceed the groundwater maximum contaminant levels for any of the cases along with chromium except for Case 7 (Table G.4). At the Columbia River shoreline, no constituent exceeded the groundwater maximum contaminant levels for any of the cases (Table G.4).

G.3.2 GROUNDWATER DATA

Based on *Hanford Site Groundwater Monitoring for Fiscal Year 2000* (Hartman et al. 2001) groundwater monitoring well data for the RCRA groundwater wells associated with WMA S-SX indicate the following constituents have exceeded the 40 CFR 141 drinking water standards during fiscal year 2000:

- Antimony
- Carbon tetrachloride
- Gross alpha
- Gross beta
- Nitrate
- Nitrite
- Technetium-99
- Tritium
- Uranium.

Table G.5 provides the RCRA groundwater monitoring well exceedances for the various constituents and the number of exceedances that have occur for the fiscal year.

Groundwater monitoring well 299-W23-19 is located inside the SX tank farm and was constructed under the RCRA facility investigation conducted in June 1999.

**Table G.5. Groundwater Monitoring Results Exceeding Maximum Contaminant Levels
or Drinking Water Standards at Waste Management Area S-SX**

Well Number	Antimony (µg/L)	Carbon Tetrachloride (µg/L)	Gross Alpha (pCi/L)	Gross Beta (pCi/L)	Nitrate (µg/L)	Nitrite (µg/L)	Technetium-99 (pCi/L)	Tritium (pCi/L)	Uranium (µg/L)
299-W22-39	NA	NA	NA	NA	NA	NA	NA	28,500 (3)	NA
299-W22-44	42.8 (1)	8.6 (5)	NA	NA	NA	NA	NA	NA	NA
299-W22-45	NA	12 (3)	NA	768 (3)	47,366.76 (2)	NA	2,080 (3)	NA	NA
299-W22-46	26.4 (1)	30 (3)	NA	1,830 (3)	45,596.04 (1)	NA	5,330 (3)	26,400 (3)	NA
299-W22-48	NA	5.6 (1)	NA	555 (2)	NA	NA	1,290 (1)	NA	NA
299-W22-49	44.3 (1)	6 (2)	NA	NA	NA	NA	NA	23,900 (3)	NA
299-W22-50	88.6 (1)	23 (5)	20.9 (1)	1,420 (4)	57,991.08 (1)	NA	4,240 (3)	31,400 (3)	NA
299-W23-1	NA	25 (1)	NA	110 (1)	NA	NA	NA	NA	NA
299-W23-13	30 (1)	11 (2)	NA	NA	NA	NA	NA	NA	NA
299-W23-14	NA	NA	NA	NA	134,574.7 (1)	NA	NA	208,000 (1)	NA
299-W23-15	NA	140 (3)	NA	NA	NA	NA	NA	NA	NA
299-W23-19	NA	30 (4)	NA	23,000 (4)	562,203.6 (6)	5,485.18 (4)	72,000* (6)	95,800 (4)	23.6 (1)
299-W23-4	NA	130 (3)	NA	NA	NA	NA	NA	NA	25.3 (3)
299-W23-9	31.7 (1)	NA	NA	56.6 (1)	165,562.3 (3)	NA	NA	502,000 (3)	20.5 (1)
DWS or MCL	6	5	15	50	45,000	3,300	900	20,000	20

Notes: Bold indicates an upgradient groundwater monitoring well. Number indicates the maximum result for that well during the monitoring period from October 1, 1999 to September 30, 2000. Parenthesis indicates the number of exceedance in the particular well. These are the results taken in March 2001.

DWS = drinking water standard (40 CFR 141).

MCL = maximum contaminant level.

NA = well did not exceed MCLs for the constituent.

G.4.0 HUMAN HEALTH RISK AND DOSE RESULTS COMPARISON TO REGULATIONS

As presented in main text Section 4.0 and in Appendix E, the peak ILCR, hazard index, and dose for the industrial worker scenario is used as the baseline for comparison purposes. The results indicate that for all compliance points at the WMA S-SX boundary the ILCR, hazard index, and dose exceed regulatory standards of 10^{-5} , 1.0, and 4 mrem/yr, respectively (Table G.6).

The ILCR exceeds the regulatory standard of 10^{-5} for all the cross-sections at the WMA S-SX boundary and Cases 1, 2, 5, 9, and 10 at the 200 West Area fence boundary. Based on current groundwater concentrations of technetium-99 in RCRA groundwater well 299-W23-19, the ILCR would be 5.1×10^{-3} for the industrial worker scenario. The regulatory standard is 1.0×10^{-5} (Table G.6).

The hazard index exceeds the regulatory standard of 1.0 for Case 1 at the WMA S-SX boundary and 200 West fence boundary compliance points. Cases 2, 9, 10, and 11 exceed the hazard index regulatory standard of 1.0 at WMA S-SX boundary (Table G.6).

Dose exceeds the regulatory standard of 4 mrem/yr for beta/photon emitters for Cases 1, 2, 9, 10, and 11 at the WMA S-SX boundary (Table G.6).

**Table 6.6. Comparison of Peak Incremental Lifetime Cancer Risk,
Hazard Index, and Dose for the Industrial Worker Scenario**

Case	Boundary					
	S-CC'	SX-DD'	SX-FF'			
1	1.15E-03	9.98E-03	2.34E-03	5.07E-05	3.94E-06	1.33E-06
9	7.70E-04	3.03E-03	1.62E-03	2.59E-05	1.99E-06	6.92E-07
10	4.36E-04	9.02E-04	1.01E-03	1.36E-05	1.03E-06	3.67E-07
11	8.82E-05	5.49E-04	2.27E-04	3.19E-06	2.35E-07	8.59E-08
1	1.16E+01	3.00E+02	1.96E+01	1.60E+00	1.24E-01	4.22E-02
2	5.35E+00	2.99E+01	9.77E+00	3.25E-01	2.45E-02	8.79E-03
9	6.29E+00	6.73E+01	1.19E+01	5.63E-01	4.29E-02	1.52E-02
10	3.08E+00	2.07E+01	6.30E+00	2.11E-01	1.57E-02	5.69E-03
11	7.67E-01	1.25E+01	1.43E+00	2.81E-02	2.04E-03	7.54E-04
1	6.91E+01	5.94E+02	1.40E+02	3.02E+00	2.35E-01	7.94E-02
2	4.61E+01	8.86E+01	9.85E+01	1.18E+00	9.10E-02	3.16E-02
9	4.63E+01	1.80E+02	9.69E+01	1.54E+00	1.18E-01	4.13E-02
10	2.61E+01	5.37E+01	6.01E+01	8.14E-01	6.17E-02	2.19E-02
11	5.29E+00	3.26E+01	1.36E+01	1.90E-01	1.40E-02	5.12E-03

G.5.0 REFERENCES

- 10 CFR 20, "Standards for Protection Against Radiation," *Code of Federal Regulations*, as amended.
- 40 CFR 141, "National Primary Drinking Water Regulations," *Code of Federal Regulations*, as amended.
- 64 FR 61615, 1999, "Hanford Comprehensive Land-Use Plan Environmental Impact Statement (HCP EIS), Hanford Site, Richland, Washington; Record of Decision (ROD)," *Federal Register*, Vol. 64, No. 218, pp 61615, November 12.
- DNFSB 94-2, 1994, *Recommendation 94-2 to the Secretary of Energy*, Defense Nuclear Facilities Safety Board, Washington, D.C.
- DOE Order 5400.5, 1993, *Radiation Protection of the Public and Environment*, U.S. Department of Energy, Washington, D.C.
- DOE, 1999, *Final Hanford Comprehensive Land-Use Plan Environmental Impact Statement*, DOE/EIS-0222F, U.S. Department of Energy, Richland Operations Office, Richland, Washington.
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- Ecology, 2001, *Dangerous Waste Portion of the RCRA Permit for the Treatment, Storage, and Disposal of Dangerous Waste Hanford Site-Wide Permit*, Rev. 7, Washington State Department of Ecology, Olympia, Washington.
- Hartman, M. J., L. F. Morasch, and W. D. Webber, *Hanford Site Groundwater Monitoring for Fiscal Year 2000*, PNNL-13404, Pacific Northwest National Laboratory, Richland, Washington.
- National Environmental Policy Act of 1969*, 42 USC 4321 et seq.
- Resource Conservation and Recovery Act of 1976*, Public Law 94-580, 90 Stat. 2795, 42 USC 901 et seq.
- WAC 173-340, "The Model Toxics Control Act Cleanup Regulation," *Washington Administrative Code*, as amended.
- WAC 173-303-645(5), "Concentration Limits," *Washington Administrative Code*, as amended.
- WAC 173-340-747, "Deriving Soil Concentrations for Ground Water Protection," *Washington Administrative Code*, as amended.

WAC 173-340-747(8), "Alternative Fate and Transport Models," *Washington Administrative Code*, as amended.

WAC 173-340-720, "Ground Water Cleanup Standards," *Washington Administrative Code*, as amended.

APPENDIX H

**QUALITY ASSURANCE/QUALITY CONTROL
REQUIREMENTS**

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APPENDIX H

QUALITY ASSURANCE QUALITY CONTROL REQUIREMENTS

Quality assurance and quality control requirements for conducting the *Resource Conservation and Recovery Act of 1976* field investigations are addressed in Appendix A of the *Phase I RCRA Facility Investigation/Corrective Measures Study Work Plan for Single-Shell Tank Waste Management Areas* (DOE-RL 2000), which is known as the master work plan. Because the *Preliminary Site-Specific SST Phase I RFI/CMS Work Plan Addendum for WMA S-SX* (Henderson 1999) was published before the master work plan, its quality assurance project plan predates that of the master work plan but is substantially similar. The major areas covered in the master work plan are as follows:

- Project management
- Measurement/data acquisition
- Assessment/oversight
- Data validation and usability
- Data quality assessment.

The project management described in the master work plan is still valid, although the company responsible for the effort has shifted (is now CH2M HILL Hanford Group, Inc.) because of contract changes. The Office of River Protection is now the U.S. Department of Energy office responsible for the tasks.

The general requirements established in the master work plan for sampling methods, sampling handling and custody, analytical methods, and field and laboratory quality control have been followed in the activities described in this document. As noted in the main text to this document, there were few deviations from the work plans on sampling and these were due to operational concerns. Other requirements had no deviations.

CH2M HILL Hanford Group, Inc. management and tank farm staffs have routinely conducted safety assessments of the waste management area S-SX *Resource Conservation and Recovery Act of 1976* field investigation. There is, at this time, no separate formal quality assurance assessment by the Tank Farm Vadose Zone Project.

Informal reviews of data validity and usability have been held, mainly as part of the determination of second- and third-tier analyses and in the preparation of this waste management area S-SX field investigation report. Similarly, only informal data quality assessments have been performed, primarily because a systematic sampling approach was used rather than a random sampling design.

REFERENCES

DOE-RL, 2000, *Phase I RCRA Facility Investigation Corrective Measures Study Work Plan for Single-Shell Tank Waste Management Areas*, DOE/RL-99-36, Rev. 1, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

Henderson, J. C., 1999, *Preliminary Site-Specific SST Phase 1 RFI/CMS Work Plan Addendum for WMA S-SX*, HNF-4380, Rev. 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

Resource Conservation and Recovery Act of 1976, Public Law 94-580, 90 Stat. 2795, 42 USC 901 et seq.

APPENDIX I

PREPARERS

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I.1.0 PREPARERS

I.1.1 OFFICE OF RIVER PROTECTION

Robert M. Yasek, Physical Scientist

B.S. Geophysics, New Mexico Institute of Mining and Technology 1984

Mr. Yasek has over 16 years of experience in leadership and management of government projects, both military and civilian. He currently serves as the DOE project manager for the Hanford **Tank** Farms Vadose Zone Project. Prior to working at Hanford, he was the DOE Lead for Thermal Testing for the DOE's Yucca Mountain Project (YMP). Additional duties at YMP included project management of borehole geophysics for the high-level waste repository program. Mr. Yasek's military experience includes project management for flight testing of advanced weapons systems for the U.S. Air Force and operations of radar and command, control and communications (C³) systems. Between military and civilian government service, Mr. Yasek worked **as** a field geophysicist for a privately-owned company, specializing in borehole geophysics.

I.1.2 CORE TEAM

Frank J. Anderson, Scientist, CH2M HILL Hanford Group, Inc.

B.S. Geological Engineering, Colorado School of Mines 1964

M.S. Geological Engineering, University of Arizona **1968**

Mr. Anderson has over 31 years of experience **as** a geological engineer, environmental consultant, government manager and professor involving environmental characterization, compliance and remediation, mining, geology, water resources development, and program and project management. He has worked **as** a consultant at five DOE sites during the past decade: Hanford and Oak Ridge reservations, Portsmouth and Paducah Gaseous Diffusion Plants, and INEEL. He has also been a manager for the U.S. Geological Survey and the U.S. Office of surface Mining, and an assistant professor of geology. Mr. Anderson was responsible for FY 2001 Interim Measures engineering design and construction activities for the **Tank** Farm Vadose Zone Project, and prepared Section 3.5 and Appendix F in this document.

Dwayne Crumpler, Senior Hydrogeologist, Jacobs Engineering Group, Inc.

B.S. Geology, Lamar University 1985

M.S. Geology, Baylor University 1989

Mr. Crumpler has over 15 years of experience in groundwater field investigations related to RCRA facility investigations and CERCLA remedial investigations at municipal landfills, Department of Defense and Department of Energy facilities. He serves **as** a Senior Geologist and Regulatory Specialist for the preparation of various RCRA and NEPA documents related to Hanford. He has conducted and analyzed seismic field studies, aquifer pumping tests and slug

tests, installed monitoring wells and soil borings, and conducted groundwater and surface-water sampling programs at DOE and DOD facilities. He has prepared the site-specific work plans associated with the Single-Shell Tanks RCRA corrective action program and has been involved in the single-shell tank retrieval program. He was the coordinator for the document and preparation of the human health risk analyses, regulatory analyses, introduction, approach, conclusions and recommendations for this document.

Thomas E. Jones

Tom Jones holds a Ph.D. in Inorganic/Analytical Chemistry from Washington State University and has over 20 years experience at Hanford in the areas of tank waste characterization, development of tank waste inventory estimates, and tank farm vadose zone investigations. Over the past four years, Dr. Jones has led the task developing tank leak inventory estimates.

Raziuddin Khaleel, Consulting Engineer, Environmental and Nuclear Initiatives, Flour Federal Services.

B.S.	Civil Engineering, Bangladesh University of Engineering and Technology	1966
M.S.	Water Science and Engineering, Asian University of Technology	1970
Ph.D.	Soil and Water Engineering, Texas A&M University	1977

Dr. Khaleel has over 30 years of experience in groundwater hydrology and numerical simulations of subsurface flow and transport. He was a key contributor to the Hanford Site solid waste PAs and the immobilized low-activity waste PA, particularly in the area of conceptual model development, direction of modeling, and in writing the document. For this document, he was responsible for creating the modeling data package, coordinating the modeling work, and writing of several sections.

Anthony J. Knepp, Manager, CH2M HILL Hanford Group, Inc.

B.S.	Engineering, Johns Hopkins University	1971
M.S.	Environmental Systems Engineering, Clemson University	1973

Anthony Knepp was responsible for the management and direction of the report including its conclusions and recommendations. Mr. Knepp has over 25 years of experience in environmental cleanup and has worked as a consulting engineer, project engineer, government manager, and project manager. His experience includes water resources planning, development of water supply systems, construction of industrial treatment facilities, and environmental characterization and cleanup. For the last 10 years, he has concentrated on remediation of radiologically contaminated groundwater and soils.

Frederick **M. Mann**, Scientist, CH2M Hill Hanford Group

B.S.	Physics, Stanford University	1970
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Dr. Mann is the team leader for the ILAW Performance Assessment activity, which is charged with preparing this document. He was the main author of the 1998 and 2001 versions of the Hanford *Immobilized Low-Activity Tank Waste Performance Assessment*. He has worked for over 25 years in the field of nuclear data and the application of those data to large energy facilities. He has advised the DOE and the International Atomic Energy Agency. He was the chief internal reviewer of the document.

David A. Myers, Scientist, CH2M HILL Hanford Group, Inc.

David Myers earned a Master of Science in geology and hydrology from the University of Idaho. He is a registered professional geologist in Idaho and Oregon. His work has focused on water resources, as well as environmental monitoring and remediation of groundwater contamination. Since arriving at the Hanford Site in 1974, Mr. Myers has provided technical support for the Site-Wide Groundwater Monitoring Program, as well as early development of the *Resource Conservation and Recovery Act of 1976* monitoring program for the low-level waste burial grounds. He served as a senior hydrogeologist within the environmental restoration program, actively participating in the design and implementation of groundwater remediation projects. He supports the ~~Tank Farm~~ Vadose Zone Project as a technical coordinator, ensuring that multiple aspects of this complex problem are integrated and coordinated. For this document, he was responsible for preparing the geology sections and field investigation activities sections in Sections 2.0 and 3.0 and Appendices B and C.

Leiloni J. Page, Sr. Technical Writer/Editor, Jacobs Engineering Group Inc.

B.A.	English, University of Idaho	1992
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Ms. Page has 11 years of technical writing and editing and document publication experience. Her experience includes 8 years of working directly with managers and senior technical staff from various disciplines on highly technical risk and safety analysis documents to provide document editing, rewriting, and reorganization expertise as needed to ensure clarity, consistency, and readability. Ms. Page also works directly with project teams to develop internal production schedules and coordinates and manages document production staff to carry out editing, word processing, and graphics generation. She was the technical information coordinator for this report and maintained and coordinated the document production schedule in addition to providing technical editing support.

R. Jeffrey Serne, Staff Scientist in PNNL's Applied Geology and Geochemistry Group

B.S.	Chemistry, University of Washington	1969
B.S.	Oceanography, University of Washington	1969

Mr. Serne currently is leading the PNNL applied geochemical research and characterization efforts supporting the Office of River Protection Vadose Zone project. The goal is to determine the distribution of contaminants that have leaked from SST's and their future fate. Mr. Serne is also lead geochemist for the near-field and the far-field geochemical studies for the proposed Immobilized Low-Activity Waste repository. Finally, Mr. Serne is a co-investigator/collaborator on 4 EMSP basic science projects pertaining to the Vadose Zone. He was lead author on the four borehole characterization reports found in the appendices of the FIR.

Harold A. Sydnor, Scientist, CH2M HILL Hanford Group, Inc.

B.S.	Geology, Western Kentucky University	1979
M.S.	Environmental Resource Management	1998

Mr. Sydnor is the team leader for characterization activities inside the single-shell tank farms. He has over **20** years of experience performing geologic and hydrogeologic investigations and evaluations in the private and public sectors. He was the field team leader for characterization activities associated with the work plan addenda.

Marcus I. Wood, Principal Scientist, Waste Management, Fluor Hanford, Inc.

B.S.	Geology, University of North Carolina	1973
Ph.D.	Geology, Brown University	1980

Dr. Wood currently is responsible for developing the PA analyses for the disposal of solid low-level waste at the Hanford Site. He is the coordinating author of the Hanford Site solid waste performance assessments and has been largely responsible for the integration **and** the interpretation of the analytical results in those documents. He has coordinated similar analyses for the Environmental Restoration Disposal Facility (ERDF), at which wastes generated in the remediation of Hanford Site waste sites regulated under the ***Comprehensive Environmental Resource Conservation and Recovery Act of 1981*** and the 200 West Area low-level burial grounds are disposed. He **has** directed numerous projects to quantify the geochemical properties of radionuclides in the Hanford Site geohydrologic environment. He also was responsible for developing a multifunctional waste package backfill material for isolating spent fuel and high-level waste. He was responsible for the conceptual model and for writing Chapters 2 and 3.

John M. Zachara, Chief Scientist VI, Pacific Northwest National Laboratory

B.S.	Chemistry and Geology, Bucknell University	1973
M.S.	Soil/Watershed Chemistry, University of Washington	1979
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Dr. Zachara is chief scientist and one of four associate scientific directors of the William R. Wiley Environmental Molecular Sciences Laboratory (EMSL) at Battelle, Pacific Northwest National Laboratory. The EMSL is a state-of-the-art U.S. Department of Energy user facility focused on environmental molecular science. Dr. Zachara employs various molecular spectroscopies, electron and scanning probe microscopies, and modeling techniques in the study of contaminant geochemistry. He has performed research on these subjects for over 25 years and is the author of over 120 scientific publications. Dr. Zachara coordinates EMSL research focused on the Hanford vadose zone, and he functioned as chief scientist for the Science and Technology piece of the S and SX tank farms study that is summarized in Appendix D.

1.1.3 PEER REVIEW TEAM

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1.1.4 SUPPORT TEAM**1.1.4.1 Field Work**

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