PNL-4773
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NUREG/CR-3554
PNL-4773

Radionuclide Migration in Groundwater

Annual Progress Report for 1982

Prepared by D. E. Robertson, A. P. Toste, K. H. Abel, R. L. Brodzinski

Pacific Northwest Laboratory
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Battelle Memorial Institute

Prepared for
U.S. Nuclear Regulatory
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Radionuclide Migration in Groundwater

Annual Progress Report for 1982

Manuscript Completed: August 1983
Date Published: January 1984

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Prepared for
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Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555
NRC FIN B2380

NUREG-0354
PML-475
RW

Radionuclide Migration in Groundwater

Annual Progress Report for 1982

Manuscript Completed: August 1983
Data Published: January 1984

Prepared by
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Prepared for
Division of Health, Safety and Waste Management
Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, D.C. 20555
NRC File 32-980

SUMMARY

Research has continued at a low-level waste disposal facility to characterize the physicochemical species of radionuclides migrating in groundwater. This facility consists of an unlined basin and connecting trench which receives effluent water containing low levels of a wide variety of fission and activation products and trace amounts of transuranic radionuclides. The effluent water percolates through the soil and a small fraction of it emerges at seepage springs located some 260 meters from the trench. The disposal basin and trench are very efficient in retaining most of the radionuclides, but trace amounts of a number of radionuclides existing in mobile chemical forms migrate in the groundwater from the trench to the springs. This facility provides the opportunity for characterizing the rates and mechanisms of radionuclide migration in groundwaters, identifying retardation processes, and validating geochemical models.

During FY 1982 three research wells were installed 30, 46 and 73 meters from the disposal trench to study the changes in chemical forms which occur as various mobile radionuclides migrate from the trench to the seepage springs. Soil cores collected during the well drilling contained very low concentrations of only those radionuclides which exist in soluble, mobile forms previously identified in the spring water. The fact that minimal accumulation of these radionuclides was observed in the soil cores indicates that once the mobile species of radionuclides have migrated from the immediate confines of the trench they do not readily adsorb to downstream soils. The depth distribution of the radionuclides in the soil at the well locations showed maximum concentrations in a relatively narrow band approximately 8 meters in width, indicating that the water is being transported from the trench to the springs in a rather narrow lens. The depth distributions of radionuclides obtained from the soil analyses were verified by in situ measurements obtained by gamma logging the research wells during their construction.

The soil textures at this facility typically consist of 77-80% as aggregate >2 mm, 17-21% sand, 0.3-2.2% silt, and 0.6-0.7% clay. The dominant minerals are quartz and feldspar which compose approximately 80% of the soils. Clay minerals consist of montmorillonite, kaolinite and illite. Other trace minerals include amphibole, biotite and calcite.

Water sampling at the trench, wells and springs conducted in January and February, 1983, revealed significant changes in the physicochemical speciation of the mobile radionuclides as they migrated from the trench to the springs. Particulate and cationic forms were efficiently retained on the soil in the immediate vicinity of the trench, while anionic and nonionic forms continued to migrate to the springs. Mobile anionic species of ^{60}Co , ^{99}Mo , $^{99\text{m}}\text{Tc}$, $^{103-106}\text{Ru}$, and ^{131}I , and nonionic forms of ^{125}Sb migrate to the springs. During the January sampling, anionic forms of ^{54}Mn , ^{59}Fe and ^{95}Nb were observed to migrate in the groundwater only as far as Well #1, a lateral distance of 30 meters from the trench. Cesium-137, ^{140}La , ^{144}Ce and ^{154}Eu were never detected in waters sampled from the wells or the springs. During the February sampling, relatively large amounts of suspended particulates were present in the trench water and traces of particulate ^{54}Mn , ^{59}Fe , ^{95}Zr , ^{137}Cs and

^{154}Eu were observed in the water from Well #1, indicating some migration of microparticulates as far as 30 meters from the trench.

Additional detailed studies of the chemical speciation of radioiodine revealed that a major fraction (49-57%) of the total ^{131}I in the trench, well, and spring waters occurred in what is presumed to be a soluble organic species. This organic form(s) behaves like an anion, and appears to be quite mobile in the groundwater. Inorganic iodide (I^-) accounted for 42 to 48% of the total ^{131}I , and iodate (IO_3^-) represented only 1 to 3% of the total.

A preliminary examination of the long-lived ^{63}Ni (100 yr.) in waters and soils from this disposal system was initiated. Substantial concentrations (0.64 to 3.3×10^5 pCi/gm) were found in the trench sediments. Readily measurable concentrations were observed in trench water, occurring mainly in particulate and cationic forms. Nickel-63 was barely detectable in spring water, and appeared to occur mainly in a nonionic form. Nickel-63 was also detected in very low concentrations in soil from the seepage spring area, indicating that traces of ^{63}Ni had migrated over 260 meters from the trench. This radionuclide is of particular interest in low-level waste management because of its long half-life and its relatively high abundance in nuclear power plant wastes.

Tritium concentrations in trench, well and spring waters (16,000 to 45,000 pCi/l) were elevated well above ambient groundwater concentrations, and serve as very useful tracers of the trench water during its transport through this system. During the January and February sampling periods, the tritium concentrations in the well and spring waters were equal to, or somewhat higher than those observed in the trench waters, indicating that the water sampled from the wells and springs was not significantly diluted by the ambient groundwater.

Chemical analyses of the trench, well and spring waters indicated that these waters are well oxygenated and contain low concentrations of dissolved organic matter. The major anions are HCO_3^- , SO_4^{2-} , NO_3^- and Cl^- , and the dominant cations are Ca^{++} , Mg^{++} and Na^+ .

Since organic complexing materials may increase the mobility of radionuclides in groundwaters, a comprehensive analysis of trench sediments for organic constituents by GC and GC/MS was conducted. These analyses identified a wide variety of hydrophilic and hydrophobic compounds. Several classes of carboxylic acids which are common metabolic intermediates and structural components of microbiota were identified at ppm and ppb concentrations. The highest concentrations of these acids were observed in sediments sampled midway down the trench. The hydrophobic organic extracts of the sediments were too complex to permit detailed GC and GC/MS analyses. However, a number of alkanes, alkenes and alkynes were observed. In addition, elemental sulfur was detected, as well as three cyclic sulfur species consisting of a five membered ring compound CH_2S_4 , a six membered ring compound CH_2S_5 , and a seven membered ring CH_2S_6 . The origin of these compounds and whether or not they can mediate the mobility of radionuclides is not presently known.

TABLE OF CONTENTS

SUMMARY	iii
CONTENTS.....	v
FIGURES	vi
TABLES	viii
1.0 Introduction	1
2.0 New Research Well Implantation	2
2.1 Description of Research Wells	2
2.2 Radionuclide Analysis of Soil Cores	2
2.3 Gamma-Logging of Wells	5
2.3.1 Calibration of Well Casing	11
2.3.2 Gamma-Logging of Research Wells	14
3.0 Chemical Species of Radionuclides in Trench, Well and Spring Waters	14
3.1 Particulate, Anionic, Cationic and Nonionic Forms	23
3.2 Radioiodine Speciation	47
3.3 Physicochemical Speciation of ^{63}Ni in Trench and Spring Waters	50
3.4 Groundwater Chemical Analyses	51
4.0 Soil Texture and Mineralogy	55
5.0 Characterization of Organic Matter in Trench Sediments	56
5.1 Sample Collection and Preparation	56
5.2 GC and GC/MS Analyses	59
5.3 Organic Constituents in Trench Sediments	60
REFERENCES	69

LIST OF FIGURES

2.1	Well Construction Schematic	3
2.2	Radionuclide Concentrations in Soil Cores from Research Well #1, September, 1982	6
2.3	Radionuclide Concentrations in Soil Cores from Research Well #2, August, 1982	9
2.4	Radionuclide Concentrations in Soil Cores from Research Well #3, September, 1982	10
2.5	Efficiency Curve for Downhole Detector for Gamma Logging of Research Wells (20 cm diameter, Schedule 40 steel casing)	13
2.6	Gamma-Ray Log of Research Well #1, September, 1982	18
2.7	Gamma-Ray Log of Research Well #2, August, 1982	19
2.8	Gamma-Ray Log of Research Well #3, August, 1982	20
2.9	Gamma-Logging of Aborted Research Well #1A, August, 1982	22
3.1	Battelle Large Volume Water Sampling Schematic	24
3.2	Change in Physicochemical Forms of ^{137}Cs During Migration in Groundwater	31
3.3	Change in Physicochemical Forms of ^{131}I During Migration in Groundwater	32
3.4	Change in Physicochemical Forms of ^{60}Co During Migration in Groundwater	33
3.5	Change in Physicochemical Forms of ^{103}Ru During Migration in Groundwater	35
3.6	Change in Physicochemical Forms of ^{125}Sb During Migration in Groundwater	36
3.7	Change in Physicochemical Forms of ^{95}Nb During Migration in Groundwater	38
3.8	Change in Physicochemical Forms of ^{59}Fe During Migration in Groundwater	39

LIST OF FIGURES (continued)

3.9	Change in Physicochemical Forms of ^{54}Mn During Migration in Groundwater	41
4.1	Photograph of a Cutaway Soil Bank Near the Study Area Showing Interstitial Sand, Silt and Clay Interspersed Between Cobbles and Boulders	57
5.1	Sampling Locations of Trench Sediments for Organic Constituent Analyses	58
5.2	Analysis Scheme for the Extraction and Analysis of Organics and Radionuclides from Trench Sediments	60
5.3	Organic Extracts of Trench Sediments	62
5.4	Classes of Carboxylic Acids Identified in the Hydrophilic Organic Fraction of the Trench Sediments	64
5.5	Elemental Sulfur in the Aqueous Extract of the Trench Sediments	66
5.6	Cyclic Sulfur Species Identified in the Trench Sediment from Manway 2	68

LIST OF TABLES

2.1	Radionuclide Concentrations in Soil Cores from Research Well #1, August, 1982	4
2.2	Radionuclide Concentrations in Soil Cores from Research Well #2, August, 1982	7
2.3	Radionuclide Concentrations in Soil Cores from Research Well #3, August, 1982	8
2.4	Nuclear Data for Generating Counting Efficiency Curve for Gamma Well Logging	12
2.5	Gamma-Logging of Research Well #1, September, 1982	15
2.6	Gamma-Logging of Research Well #2, August, 1982	16
2.7	Gamma-Logging of Research Well #3, August, 1982	17
2.8	Gamma-Logging of Aborted Research Well #1A, August, 1982	21
3.1	Radionuclide Concentrations and Physicochemical Forms in Trench Water, January, 1983	25
3.2	Radionuclide Concentrations and Physicochemical Forms in Water from Well #1, January, 1983	27
3.3	Radionuclide Concentrations and Physicochemical Forms in Water from Well #3, January, 1983	28
3.4	Radionuclide Concentrations and Physicochemical Forms in Spring Water, January, 1983	29
3.5	Radionuclide Concentrations and Physicochemical Forms in Trench Water, February, 1983	43
3.6	Radionuclide Concentrations and Physicochemical Forms in Trench Water, February, 1983	44
3.7	Radionuclide Concentrations and Physicochemical Forms in Water from Well #1, February, 1983	45

LIST OF TABLES (continued)

3.8	Radionuclide Concentrations and Physicochemical Forms in Water from Well #3, February, 1983	46
3.9	Radionuclide Concentrations and Physicochemical Forms in Spring Water, February, 1983	48
3.10	Chemical Speciation of Radioiodine in Trench, Well, and Spring Waters	49
3.11	Nickel-63 Concentrations and Chemical Speciation, June, 1981	50
3.12	Chemical Composition of Trench, Well, and Spring Waters, January, 1983	52
3.13	Chemical Composition of Trench, Well, and Spring Waters, February, 1983	54
4.1	Grain Size Analysis of Soils Sampled from a Cutaway Soil Bank Between the Trench and Springs	56
5.1	Hydrophilic Organics in Trench Sediments	63

LIST OF TABLES (continued)

3.8	Radionuclide Concentrations and Physicochemical Forms in Water from Well #3, February, 1983	46
3.9	Radionuclide Concentrations and Physicochemical Forms in Spring Water, February, 1983	48
3.10	Chemical Speciation of Radionuclides in Trench, Well, and Spring Waters	49
3.11	Nickel-63 Concentrations and Chemical Speciation, June, 1981	50
3.12	Chemical Composition of Trench, Well, and Spring Waters, January, 1983	52
3.13	Chemical Composition of Trench, Well, and Spring Waters, February, 1983	54
4.1	Grain Size Analysis of Soils Sampled from a Cutaway Soil Bank Between the Trench and Springs	56
5.1	Hydrophilic Organics in Trench Sediments	63

One of the problems faced today by the nuclear industry is the disposal of both high-level and low-level radioactive wastes which have been and will continue to be generated. Although research into waste management technology has greatly accelerated during the past several years, many uncertainties still exist regarding the environmental and geochemical behavior and fate of buried nuclear wastes.

One of the major gaps in understanding the environmental behavior of the long-lived radionuclides associated with low and high-level waste is the lack of an adequate knowledge of the mechanisms by which these radionuclides are mobilized and transported in groundwaters. Predictions of the rate of movement of radionuclides in groundwaters, based on laboratory-derived K_d values, can lead to erroneous conclusions concerning the groundwater mobility of various radionuclides. This is because laboratory-derived K_d values have been obtained using ideal soluble tracers which were probably not in the same physicochemical form(s) as the mobile radionuclide species known to be present in some groundwaters. In addition, the K_d experiments have not considered the long-term leaching of soil-adsorbed radionuclides by ligands and complexing substances contained in groundwaters. To better understand the rates and mechanisms of radionuclide transport in groundwaters, it is necessary to examine such transport in actual situations and compare the observed behavior with the predicted rate of movement.

The objectives of this research program are to utilize a mildly contaminated groundwater plume as a natural laboratory for: 1) identifying what specific physicochemical forms of the long-lived radionuclides are migrating; 2) determining the rates and mechanisms of radionuclide migration during groundwater transport; and 3) comparing the actual transport rates observed in this aqueous disposal system with predicted rates based on geochemical modeling. These studies are helping to provide a sound basis for understanding the mechanisms of groundwater transport of radionuclides. The information that is generated can be used in formulating guidelines for operation of existing low level waste disposal sites, in determining essential requirements for remedial action and decommissioning, in determining what long-term surveillance and maintenance needs will be required and in developing criteria for selection of future burial sites.

The long-lived radionuclides specified in 10 CFR 61 are being emphasized in this investigation, including ^{60}Co , ^{63}Ni , ^{90}Sr , ^{99}Tc , ^{106}Ru , ^{125}Sb , ^{129}I , ^{137}Cs and $^{152,154,155}\text{Eu}$. In addition, a large number of short- and intermediate-lived radionuclides can also be studied. The transuranic radionuclides, principally $^{239-240}\text{Pu}$, are also being studied under a companion program.

2.0 New Research Well Placement

Past studies have been limited by accessible sampling points at only the inlet to the trench and at the seepage springs. In order to study the system in more detail to observe the changes in chemical speciation which occur as a function of distance as the groundwater moves through the soil, a series of three new sampling wells were installed during FY 1982 between the trench and the springs.

2.1 Description of Research Wells

In August, 1982, three research wells were drilled at distances of approximately 30, 46, and 73 meters away from the trench. The wells were drilled in a radiation zone, and slightly radioactively contaminated soils were encountered, requiring a constant radiation monitoring coverage during the entire drilling phase. Because the wells were drilled into glaciofluvial unconsolidated deposits which contained a significant fraction of large aggregate (up to 10-20 cm in diameter), the cable tool method of drilling was utilized. Twenty-centimeter diameter temporary steel-cased wells were drilled to depths of about 5 to 13 meters below the saturated zone of the perched water table. Total well depths ranged from about 21 to 30 meters. Two 5-cm diameter schedule 40 PVC pipes with screened, open ends were inserted into the 20-cm diameter temporary casing at two depths within the saturated zone, and the wells were completed as shown in Figure 2.1. The well finally drilled closest to the trench had to be shifted about 10 meters north of the alignment of the middle and farthest well because of drilling difficulties encountered at the original position. Drilling at the original aligned location was terminated at a depth of 7.5 meters when some impenetratable object was encountered. The object appeared to be metallic and relatively high levels of ^{54}Mn , ^{60}Co and ^{137}Cs were observed. The water depth in the wells varied from 16.2 to 18.0 meters.

During the well drilling, soil samples were collected every 1.5 meters, and upon completing the temporary 20-cm steel casing, the wells were logged with a specially designed gamma-ray detector/spectrometer.

2.2 Radionuclide Analyses of Soil Cores

The soil samples collected every 1.5 meters during the drilling operations were dried and cobble-sized aggregate was removed by hand-picking. Approximately 300-400 gm of weighed aliquots of soil were then packaged in a standard counting geometry and gamma-counted on a Ge(Li) gamma-ray spectrometer.

At research well #1, located approximately 30 meters from the trench, very low concentrations of ^{54}Mn , ^{60}Co , $^{103-106}\text{Ru}$, ^{125}Sb and ^{137}Cs were detectable by direct gamma-ray spectrometry (see Table 2.1). These radionuclides peaked in concentration in

FIGURE 2.1. Well Construction Schematic

TABLE 2.1. Radionuclide Concentrations in Soil Cores from
Research Well #1, August 1982

RADIONUCLIDE CONCENTRATIONS IN SOIL (pCi/gm)								
DEPTH (m)	⁴⁰ K	⁵⁴ Mn	⁶⁰ Co	¹⁰³ Ru	¹⁰⁶ Ru	¹²⁵ Sb	¹³⁷ Cs	²¹⁴ Pb
1.5	9.30 ± 0.15	0.063 ± 0.006	0.598 ± 0.011	0.019 ± 0.011	<0.04	0.115 ± 0.014	0.684 ± 0.009	0.408 ± 0.011
3.0	10.3 ± 0.15	0.043 ± 0.005	0.745 ± 0.012	0.012 ± 0.011	<0.04	0.145 ± 0.014	0.746 ± 0.009	0.428 ± 0.011
4.6	10.3 ± 0.20	0.053 ± 0.007	0.779 ± 0.016	0.026 ± 0.014	<0.05	0.131 ± 0.018	0.671 ± 0.012	0.424 ± 0.014
6.1	7.58 ± 0.14	0.050 ± 0.005	0.836 ± 0.013	<0.011	<0.04	0.194 ± 0.014	0.735 ± 0.010	0.385 ± 0.011
7.6	8.21 ± 0.16	0.024 ± 0.006	0.906 ± 0.014	0.016 ± 0.013	0.064 ± 0.046	0.189 ± 0.016	0.548 ± 0.009	0.400 ± 0.012
9.1	4.74 ± 0.15	0.203 ± 0.008	2.17 ± 0.020	<0.014	0.063 ± 0.052	0.102 ± 0.016	0.631 ± 0.011	0.375 ± 0.012
10.7	10.08 ± 0.16	0.019 ± 0.005	0.229 ± 0.0067	<0.013	<0.04	<0.013	0.258 ± 0.007	0.441 ± 0.011
12.2	8.16 ± 0.14	0.206 ± 0.008	2.17 ± 0.019	<0.017	<0.05	0.057 ± 0.018	0.772 ± 0.010	0.668 ± 0.014
13.4	8.93 ± 0.14	0.149 ± 0.008	3.06 ± 0.022	0.043 ± 0.019	0.382 ± 0.059	0.901 ± 0.022	0.911 ± 0.011	0.313 ± 0.013
13.7	8.52 ± 0.16	0.521 ± 0.015	9.90 ± 0.043	0.253 ± 0.035	1.60 ± 0.11	2.99 ± 0.039	1.15 ± 0.01	0.376 ± 0.021
15.2	8.41 ± 0.15	0.383 ± 0.013	9.00 ± 0.040	0.163 ± 0.033	1.39 ± 0.10	2.91 ± 0.036	0.488 ± 0.011	0.347 ± 0.019
16.8	9.57 ± 0.15	0.658 ± 0.015	10.5 ± 0.044	0.185 ± 0.038	1.47 ± 0.11	3.13 ± 0.041	3.96 ± 0.02	0.362 ± 0.021
18.3	10.7 ± 0.16	0.143 ± 0.011	6.56 ± 0.035	0.162 ± 0.031	1.20 ± 0.09	2.25 ± 0.033	0.641 ± 0.011	0.389 ± 0.018
20.4	13.3 ± 0.18	0.043 ± 0.009	4.38 ± 0.029	0.191 ± 0.028	1.30 ± 0.08	1.76 ± 0.029	0.211 ± 0.008	0.454 ± 0.016

the depth interval between 13.5 to 18.5 meters which corresponded with the depth of water saturation (see Figure 2.2). The water depth in well #1 at the time the well was drilled was 17.1 meters. The water level has since stabilized at a depth of 16.2 meters. The very low radionuclide concentrations attached to the soil removed from well #1 indicates that the 30 meters of soil between the trench and the well has been quite efficient during the past 18 years of usage in retarding the migration of most radionuclides. Except for ^{54}Mn and ^{137}Cs , the only other gamma-emitting radionuclides observed on the soil were those which have been shown to possess mobile chemical forms which eventually migrate over 200 meters to the seepage springs, e.g. ^{60}Co , ^{106}Ru and ^{125}Sb .

Average concentrations of ^{54}Mn , ^{60}Co and ^{137}Cs in the trench soils were reported to be 7.0×10^5 , 1.5×10^7 and 6.6×10^5 pCi/gm, respectively, during 1982(1). The maximum concentrations of ^{54}Mn , ^{60}Co and ^{137}Cs in soils from well #1 amounted to 0.66, 10.5 and 3.96 pCi/gm, respectively. This represents decontamination factors of 1.1×10^6 , 1.4×10^6 and 1.7×10^5 , respectively, for ^{54}Mn , ^{60}Co and ^{137}Cs afforded by the 30 meter soil column between the trench and well #1.

In wells #2 and #3, the ^{54}Mn and ^{137}Cs were non-detectable in the soils removed from the saturated zone, and the only detectable long-lived gamma emitters were ^{60}Co , ^{103}Ru , ^{106}Ru and ^{125}Sb (see Tables 2.2 and 2.3). These radionuclides peaked in concentration at depths approximately corresponding to the present water levels in the wells (see Figures 2.3 and 2.4). The maximum ^{60}Co concentration was 1.5 pCi/gm in these soils, while ^{54}Mn (<0.009 pCi/gm) and ^{137}Cs (<0.005 pCi/gm) were non-detectable. This represents decontamination factors of $>7.8 \times 10^7$, 1.0×10^7 and $>1.3 \times 10^8$, respectively, for ^{54}Mn , ^{60}Co and ^{137}Cs .

The depths of maximum radionuclide concentrations in the soil correlate with the approximate depth of water saturation in the wells. This suggests that the water flowing from the trench to the seepage springs is primarily transported in a lens of flow some 8 to 10 meters in breadth beginning at the level of saturation.

2.3 Gamma-Logging of Wells

To determine the in situ concentrations of radionuclides in the soil column between the trench and the springs, and to verify the soil core radionuclide analyses, the three research wells were logged for gamma emitting radionuclides. The logging was performed while the 20 cm diameter, schedule 40 steel casing was temporarily in place. A special calibration was performed to obtain an efficiency vs. gamma-ray energy curve for gamma-logging through the 20 cm diameter, schedule 40 steel casing.

FIGURE 2.2. Radionuclide Concentrations in Soil from Research Well #1, September, 1982

TABLE 2.2. Radionuclide Concentrations in Soil Cores from Research Well #2, August, 1982

RADIONUCLIDE CONCENTRATIONS IN SOIL (pCi/gm)								
DEPTH (m)	⁴⁰ K	⁵⁴ Mn	⁶⁰ Co	¹⁰³ Ru	¹⁰⁶ Ru	¹²⁵ Sb	¹³⁷ Cs	²¹⁴ Pb
1.5	9.75 ± 0.18	0.008 ± 0.005	0.065 ± 0.007	<0.008	<0.04	<0.013	0.014 ± 0.005	0.432 ± 0.012
3.0	8.95 ± 0.18	0.013 ± 0.004	0.065 ± 0.006	<0.008	<0.04	<0.013	0.018 ± 0.005	0.448 ± 0.012
4.6	7.26 ± 0.14	0.013 ± 0.004	0.067 ± 0.006	<0.006	0.061 ± 0.031	<0.010	0.008 ± 0.004	0.319 ± 0.009
6.4	11.41 ± 0.23	<0.006	0.014 ± 0.008	<0.01	<0.05	0.041 ± 0.017	0.015 ± 0.007	0.519 ± 0.016
7.6	7.26 ± 0.15	<0.004	0.018 ± 0.005	<0.007	<0.03	<0.014	0.012 ± 0.004	0.303 ± 0.009
9.1	6.38 ± 0.28	<0.007	0.017 ± 0.009	<0.01	<0.06	<0.019	<0.007	0.359 ± 0.018
10.7	6.60 ± 0.13	<0.006	0.005 ± 0.005	<0.006	<0.03	<0.010	0.015 ± 0.004	0.324 ± 0.008
12.2	7.53 ± 0.12	<0.003	<0.004	<0.006	<0.03	<0.010	0.010 ± 0.003	0.331 ± 0.008
14.0	8.28 ± 0.16	<0.004	0.025 ± 0.005	<0.007	<0.03	<0.010	<0.004	0.356 ± 0.009
15.2	8.13 ± 0.16	<0.004	0.227 ± 0.009	<0.008	<0.04	0.062 ± 0.012	<0.004	0.322 ± 0.011
16.8		<0.02	0.957 ± 0.066	<0.04	<0.23	0.623 ± 0.084	<0.02	0.349 ± 0.053
18.3	10.3 ± 0.21	<0.007	1.22 ± 0.02	0.024 ± 0.011	0.157 ± 0.058	0.707 ± 0.023	<0.006	0.363 ± 0.015
19.8	9.47 ± 0.48	<0.01	0.905 ± 0.039	<0.03	0.255 ± 0.123	0.647 ± 0.051	<0.01	0.331 ± 0.032
21.3	9.99 ± 0.78	<0.02	0.623 ± 0.055	0.116 ± 0.044	<0.19	0.640 ± 0.083	<0.02	0.339 ± 0.050
22.9	11.6 ± 0.88	<0.03	1.48 ± 0.08	<0.05	0.60 ± 0.25	0.938 ± 0.099	<0.02	0.416 ± 0.060
24.4	10.6 ± 0.77	<0.03	0.654 ± 0.057	<0.04	<0.2	0.519 ± 0.082	<0.02	0.384 ± 0.054
25.9	8.83 ± 0.76	<0.02	0.160 ± 0.036	<0.04	<0.2	0.273 ± 0.059	<0.02	0.278 ± 0.045
27.4	9.07 ± 0.71	<0.03	0.185 ± 0.037	<0.03	<0.2	0.255 ± 0.059	<0.02	0.395 ± 0.049
28.9	9.47 ± 0.73	<0.02	0.166 ± 0.036	<0.06	<0.2	0.192 ± 0.061	<0.02	0.371 ± 0.048
30.5	10.8 ± 0.18	<0.006	0.211 ± 0.008	<0.008	0.078 ± 0.040	0.142 ± 0.014	0.0434 ± 0.0047	0.408 ± 0.011

TABLE 2.3. Radionuclide Concentrations in Soil Cores from Research Well #3, August, 1982

RADIONUCLIDE CONCENTRATIONS IN SOIL (pCi/gm)								
DEPTH (m)	⁴⁰ K	⁵⁴ Mn	⁶⁰ Co	¹⁰³ Ru	¹⁰⁶ Ru	¹²⁵ Sb	¹³⁷ Cs	²¹⁴ Pb
1.5	7.10 ± 0.14	0.006 ± 0.004	0.054 ± 0.006	<0.004	<0.03	<0.010	0.023 ± 0.004	0.366 ± 0.009
3.0	7.19 ± 0.15	<0.004	0.019 ± 0.005	<0.005	<0.03	<0.010	0.017 ± 0.004	0.361 ± 0.009
4.6	5.91 ± 0.24	<0.006	0.019 ± 0.008	<0.009	<0.05	0.028 ± 0.017	0.025 ± 0.007	0.314 ± 0.016
6.1	2.39 ± 0.13	<0.003	0.006 ± 0.005	<0.007	<0.03	<0.010	0.009 ± 0.003	0.344 ± 0.009
7.6	5.48 ± 0.13	<0.003	0.009 ± 0.004	<0.005	<0.03	<0.010	<0.003	0.326 ± 0.008
9.1	4.83 ± 0.12	<0.003	0.009 ± 0.004	<0.005	<0.03	<0.009	0.009 ± 0.003	0.337 ± 0.008
10.9	1.95 ± 0.13	<0.004	0.008 ± 0.004	<0.006	<0.03	<0.010	<0.004	0.348 ± 0.009
12.5	5.91 ± 0.15	<0.005	0.009 ± 0.005	<0.006	<0.03	<0.010	<0.004	0.338 ± 0.009
13.7	1.24 ± 0.15	<0.005	0.009 ± 0.005	<0.008	<0.03	<0.010	<0.004	0.385 ± 0.009
15.2	5.92 ± 0.14	<0.004	0.200 ± 0.007	<0.006	<0.04	0.033 ± 0.010	<0.004	0.376 ± 0.009
17.1	2.04 ± 0.16	<0.007	0.392 ± 0.010	<0.008	<0.04	0.112 ± 0.013	<0.004	0.323 ± 0.010
18.3	0.721 ± 0.14	<0.008	0.678 ± 0.011	<0.0092	<0.04	0.372 ± 0.014	<0.004	0.354 ± 0.009
19.8	4.36 ± 0.15	<0.009	1.55 ± 0.02	0.037 ± 0.010	0.278 ± 0.044	0.880 ± 0.018	<0.004	0.353 ± 0.011
21.3	3.55 ± 0.18	<0.006	1.51 ± 0.02	0.034 ± 0.013	0.367 ± 0.058	1.12 ± 0.024	<0.005	0.352 ± 0.014
22.9	4.48 ± 0.15	<0.004	0.366 ± 0.009	0.025 ± 0.009	0.0969 ± 0.036	0.390 ± 0.014	<0.004	0.381 ± 0.010
24.4	1.91 ± 0.15	<0.004	0.223 ± 0.007	0.024 ± 0.009	<0.04	0.265 ± 0.013	<0.004	0.363 ± 0.009
25.9	8.42 ± 0.19	<0.005	0.165 ± 0.009	<0.011	<0.05	0.119 ± 0.015	<0.005	0.362 ± 0.012
27.4	6.76 ± 0.17	<0.005	0.141 ± 0.007	<0.011	<0.04	0.094 ± 0.013	<0.004	0.384 ± 0.011
28.9	6.54 ± 0.14	<0.004	0.093 ± 0.006	<0.009	<0.03	0.031 ± 0.010	<0.004	0.368 ± 0.009
30.5	5.95 ± 0.14	<0.005	0.159 ± 0.007	<0.006	<0.05	0.037 ± 0.010	<0.004	0.392 ± 0.009

FIGURE 2.3. Radionuclide Concentrations in Soil Cores from Research Well #2, August, 1982

FIGURE 2.4. Radionuclide Concentrations in Soil Cores from Research Well #3, September, 1982

2.3.1 Calibration of Well Casing

Since it is virtually impossible to construct a calibration facility representing an infinite volume of homogeneously contaminated undisturbed sediments, and since it is impractical to artificially generate large volumes of contaminated sediments in order to characterize those already inadvertently contaminated zones, a different approach to the development of a calibration facility was taken. A suitable pristine area which had never been tilled or disturbed in any other way by man was located. This area was designated the Natural Activities Calibration Facility and was appropriately marked to prevent inadvertent intrusion⁽²⁾. The soil texture at this location is coarse, well-sorted sand previously deposited by wind action. The surface vegetation and soil were previously sampled using a statistically acceptable geometrical pattern, and the samples were carefully analyzed in the laboratory for all measurable radionuclides. The only radionuclides present were primordial ^{40}K , uranium and thorium and their progeny, and a trace of ^{137}Cs attributed to fallout. The concentrations of the primordial activities indicated the site was spatially homogeneous to an accuracy of $\pm 8.3\%$. A 20 cm diameter by 2 m long schedule 40 steel well casing was inserted near the center of the site by means of vacuum coring, and the core material was collected in 15 cm intervals. Samples of each 15 cm layer were also analyzed in the laboratory, and the primordial radionuclide concentrations were consistent within $\pm 5.7\%$. The known concentrations of homogeneously distributed radionuclides (see Table 2.4) were used to generate an empirical efficiency curve as a function of photon energy for our well logging system. The efficiency curve is shown in Figure 2.5.

Only those naturally occurring radionuclides which were not the progeny of gaseous ^{222}Rn were used in constructing the calibration curve so that disequilibria caused by radon emanation from the soil was not a problem. These included ^{40}K , ^{208}Tl , ^{212}Pb , and ^{212}Bi .

The detector which was calibrated and used for the well logging was a 108-cm³ closed ended coaxial intrinsic germanium diode having a full-width-at-half-maximum resolution of 1.83 keV at 1332 keV. The crystal is housed in a 7.30-cm outside-diameter stainless-steel canister which also contains the necessary signal processing electronics and a spillproof liquid nitrogen cryostat providing a 12-hour holding time. The canister has a 2.54-cm screw stud at the diode end, to which 14-cm outside-diameter lead collimators or shields can be attached for the purpose of selecting quantities of gamma radiation or solid angles of interrogation.

The diode assembly is lowered into the calibration and sampling wells by means of a hand winch and stainless steel cable. Detector depth is measured to an accuracy of 1 cm with a steel measuring tape fastened to the canister. Electronic signals are

TABLE 2.4. Nuclear Data used for Generating Counting Efficiency Curve for Gamma Well Logging

RADIONUCLIDE	GAMMA ENERGY (keV)	γ/D	CONCENTRATION IN SOIL (dpm/gm)	γ pm/gm/cpm	dpm/gm/cpm	$\pm$ %
^{212}Pb	238.6	0.483	1.599	0.0386	0.0799	2.4
^{208}Tl	583.1	0.835	0.576	0.0394	0.0471	2.3
^{212}Bi	727.3	0.0721	1.599	0.0425	0.589	7.9
^{40}K	1460.8	0.105	32.78	0.0517	0.493	0.6
^{208}Tl	2614.5	0.942	0.576	0.0851	0.0903	2.5

FIGURE 2.5. Efficiency Curve for the Downwell Diode at the NACF as a Function of Gamma-Ray Energy (20 cm diameter, Schedule 40 Steel Casing)

stored in a multichannel analyzer, and power is supplied by a portable gasoline generator. Accumulated data are printed out on paper tape for evaluation and manual data reduction, and are also stored on magnetic tape for computer analysis and spectral deconvolution.

Counting intervals at each selected depth ranged from 500-1000 minutes at the calibration well to 16.67 minutes at the sampling wells.

2.3.2 Gamma Logging of Research Wells

As each temporary 20 cm diameter steel casing was completed to the desired depth, the well was logged for gamma-emitting radionuclides. The detector system, described in the previous section, was lowered into each well and 1000 second counts were made at depth intervals of 1.5 meters.

The results of the gamma logging of the research wells generally confirmed the depth distribution of radionuclides determined from the soil core measurements described in Section 2.3.1. Very low radionuclide concentrations were observed in the soil profiles down to depths of several meters above the level of water saturation. See Tables 2.5-2.7. Cobalt-60, ^{103}Ru , ^{125}Sb and ^{131}I could be detected near the saturated level in each well. Cesium-137 was detectable only in the upper 9 meters of Well #1. In Well #1 the ^{60}Co concentrations in the soil appeared to peak slightly above the saturated zone, whereas in Wells #2 and #3 the maximum concentrations occurred near the saturated level (see Figures 2.6-2.8). Also, in Well #1, a significant increase in the ^{60}Co and ^{137}Cs was observed at a depth of 4.6 meters which was not observed in the soil core analyses.

As mentioned in Section 2.1, Well #1A was aborted after reaching a depth of 7.6 meters because of impenetratable material encountered at that depth which appeared to be metallic because of the presence of metal filings in the soil core material. The concentrations of ^{54}Mn , ^{60}Co and ^{137}Cs increase sharply with depth below about 5 meters (see Table 2.8 and Figure 2.9). At a depth of 7.6 meters the ^{54}Mn , ^{60}Co and ^{137}Cs concentrations were 182, 273 and 1836 pCi/gm, respectively, and appeared to be continuing to increase. The source of these anomalously high concentrations is unknown.

3.0 Chemical Species of Radionuclides in Trench, Well and Spring Waters

During January and February, 1983, water was sampled at the trench, research wells and the seepage springs to determine the physicochemical partitioning of radionuclides between particulate forms and soluble cationic, anionic and nonionic species. A special sampling technique is utilized in which water is pumped directly from the trench, wells and springs through assemblies

TABLE 2.5. Gamma Logging of Research Well #1, September, 1982

RADIONUCLIDE CONCENTRATION IN SOIL (pCi/gm)						
DEPTH (m)	^{40}K	^{60}Co	^{103}Ru	^{137}Cs	^{131}I	^{125}Sb
1.5	11.73 $\pm$ 0.40	0.447 $\pm$ 0.028	<0.03	0.077 $\pm$ 0.020	0.074 $\pm$ 0.038	0.13 $\pm$ 0.09
3.0	12.31 $\pm$ 0.45	0.086 $\pm$ 0.020	<0.04	0.123 $\pm$ 0.028	<0.05	<0.1
4.6	11.36 $\pm$ 0.41	3.68 $\pm$ 0.04	<0.04	2.46 $\pm$ 0.06	<0.1	<0.2
6.1	12.84 $\pm$ 0.41	1.53 $\pm$ 0.08	<0.04	1.40 $\pm$ 0.05	<0.05	0.26 $\pm$ 0.11
7.6	10.00 $\pm$ 0.39	0.608 $\pm$ 0.035	<0.04	1.02 $\pm$ 0.05	0.040 $\pm$ 0.037	<0.1
9.1	11.09 $\pm$ 0.40	0.154 $\pm$ 0.022	<0.04	<0.03	<0.05	<0.1
10.7	12.04 $\pm$ 0.40	0.107 $\pm$ 0.020	<0.04	<0.03	<0.05	<0.1
12.2	13.55 $\pm$ 0.45	11.01 $\pm$ 0.13	<0.1	<0.1	<0.1	0.69 $\pm$ 0.35
13.7	12.37 $\pm$ 0.44	10.45 $\pm$ 0.12	<0.1	<0.1	0.69 $\pm$ 0.16	1.97 $\pm$ 0.40
15.2	11.81 $\pm$ 0.43	7.70 $\pm$ 0.10	<0.1	<0.1	0.72 $\pm$ 0.19	1.00 $\pm$ 0.46
17.1 (SAT'D)	11.51 $\pm$ 0.41	7.28 $\pm$ 0.10	0.27 $\pm$ 0.10	<0.1	7.61 $\pm$ 0.14	1.56 $\pm$ 0.33

TABLE 2.6. Gamma Logging of Research Well #2, August, 1982

RADIONUCLIDE CONCENTRATION IN SOIL (pCi/gm)						
DEPTH (m)	^{40}K	^{60}Co	^{103}Ru	^{137}Cs	^{131}I	^{125}Sb
3.0	10.27 ± 0.39	0.045 ± 0.018	<0.02	<0.03	<0.03	<0.06
4.6	10.08 ± 0.39	0.032 ± 0.018	<0.02	<0.03	<0.03	<0.06
6.1	9.89 ± 0.38	0.054 ± 0.018	<0.02	<0.03	<0.03	<0.06
7.6	9.44 ± 0.37	0.014 ± 0.014	<0.02	<0.03	<0.03	<0.06
9.1	10.10 ± 0.37	0.025 ± 0.014	<0.2	<0.02	<0.05	0.194 ± 0.076
10.7	11.10 ± 0.39	0.023 ± 0.018	<0.03	<0.02	<0.03	<0.07
12.2	11.51 ± 0.40	0.031 ± 0.014	<0.03	<0.02	<0.02	<0.08
13.7	11.05 ± 0.41	0.028 ± 0.016	0.040 ± 0.026	<0.03	<0.03	<0.08
15.2	11.45 ± 0.40	0.71 ± 0.034	<0.03	<0.03	<0.04	0.27 ± 0.11
16.8 (SAT'D)	14.24 ± 0.45	0.929 ± 0.039	0.19 ± 0.04	<0.03	1.26 ± 0.06	1.10 ± 0.14

TABLE 2.7. Gamma Logging of Research Well #3, August, 1982

RADIONUCLIDE CONCENTRATION IN SOIL (pCi/gm)						
DEPTH (m)	^{40}K	^{60}Co	^{103}Ru	^{137}Cs	^{131}I	^{125}Sb
4.5	10.97 ± 0.39	<0.015	<0.022	<0.02	<0.03	<0.08
6.1	11.23 ± 0.39	0.019 ± 0.014	0.067 ± 0.024	<0.02	0.05 ± 0.03	<0.08
7.6	10.70 ± 0.38	0.014 ± 0.014	<0.022	<0.02	<0.03	<0.08
10.7	11.57 ± 0.40	<0.014	<0.022	<0.02	<0.03	<0.07
12.2	12.13 ± 0.41	<0.015	<0.023	<0.02	<0.03	0.15 ± 0.08
13.7	13.18 ± 0.42	<0.014	<0.024	<0.01	<0.03	<0.08
15.2	12.50 ± 0.42	0.377 ± 0.026	0.032 ± 0.027	<0.02	<0.04	<0.09
16.8	13.24 ± 0.43	0.676 ± 0.034	<0.031	0.052 ± 0.027	<0.04	<0.09
18.3	13.60 ± 0.43	1.44 ± 0.05	0.081 ± 0.037	<0.03	0.96 ± 0.06	0.99 ± 0.13
19.8	15.04 ± 0.45	2.34 ± 0.05	<0.041	<0.03	1.24 ± 0.07	1.39 ± 0.15
21.0 (SAT'D)	12.05 ± 0.42	1.64 ± 0.05	<0.056	<0.03	2.94 ± 0.09	1.35 ± 0.15

FIGURE 2.6. Gamma-Ray Log of Research Well #1, September, 1982

FIGURE 2.7. Gamma-Ray Log of Research Well #2, August, 1982

FIGURE 2.8. Gamma-Ray Log of Research Well #3, August, 1982

TABLE 2.8. Gamma Logging of Aborted Research Well #1A,
August, 1982

RADIONUCLIDE CONCENTRATION IN SOIL (pCi/gm)

<u>DEPTH (m)</u>	<u>⁵⁴Mn</u>	<u>⁶⁰Co</u>	<u>¹³⁷Cs</u>
1.5	0.784	3.54	6.64
3.0	0.866	12.2	12.3
4.6	1.07	1.71	11.0
6.1	49.8	169	323
7.6	182	273	1836

FIGURE 2.9. Gamma-Ray Log of Aborted Research Well #1A

containing membrane filters, ion exchange resins and activated aluminum oxide beds.

A typical system is shown in Figure 3.1. Ten to twenty liters of trench water are pumped at a flow rate of about 0.5 to 1 liters/minute through a 0.4 μ Nuclepore membrane filter. The filtered water then passes directly through a 2.5 cm thick x 15 cm diameter bed of cation exchange resin (Dowex 50 x 8, H⁺ form, 200 mesh), a 2.5 cm thick x 15 cm diameter bed of anion exchange resin (Dowex 1 x 8 Cl⁻ form, 200 mesh), and then through a 0.7 cm thick x 15 cm diameter bed of fine grained activated aluminum oxide. The filters remove the particulate forms of the radionuclides, the resins remove soluble cationic and anionic species, and the activated aluminum oxide removes nonionic species.

When sampling the wells and springs, larger versions of this assembly are used to sample much greater volumes of water, since the radionuclide concentrations are much lower. Typically, 1000 to 5000 liters of spring water are pumped at a flow rate of 4-8 liters/minute through a cartridge-type, large surface area 0.4 μ Nuclepore filter and then directly through two 2.5 cm thick x 30 cm diameter beds of cation resin, two similar beds of anion resin and two 0.7 cm thick beds of activated aluminum oxide. The multiple beds are used to insure that breakthrough of the resin and aluminum oxide beds has not occurred due to saturation of the first bed.

Because of pumping rate limitations from the 5 cm diameter research wells, much smaller volumes of water (typically 100-150 liters) were sampled. This problem is being rectified by the development of a new, larger volume pumping system. The water pumped from the wells is processed the same as described above, except through slightly smaller diameter resin and Al₂O₃ beds.

3.1 Particulate, Anionic, Cationic and Nonionic Forms

Previous work at the trench/springs system has shown that the migrating radionuclide species are those which occur in anionic or nonionic forms(3,4). With the installation of the research wells between the trench and the springs, the opportunity is now available to study the change in chemical speciation of the various radionuclides in the system as the groundwater migrates from the trench to the seepage springs, a distance of some 260 meters.

The results of the water sampling conducted in January and February, 1983 are presented in Tables 3.1 to 3.9.

January, 1983 Sampling

In January, 1983, waters from the trench, Well #1, Well #3, and the seepage springs were pumped through the large volume water samplers as described in section 3.D. A wide spectrum of fission and activation products was present in the trench water (see Table 3.1). The concentrations of each radionuclide are

FIGURE 3.1. Battelle Large Volume Water Sampler Schematic

TABLE 3.1. Radionuclide Concentrations and Physicochemical Forms in Trench Water (January, 1983)

TRENCH - MANWAY #1 (1/26/83 @ 1400)					
RADIONUCLIDE	TOTAL pCi/l	% PARTICULATE	% CATIONIC	% ANIONIC	% NONIONIC
⁵⁴ Mn	109,900	11.8	87.6	0.6	0.002
⁵⁹ Fe	57,030	96.7	2.3	1.0	0.02
⁵⁸ Co	3,670	23.0	76.3	0.5	<0.02
⁶⁰ Co	49,330	58.5	41.3	0.1	0.03
⁹⁵ Zr	11,230	90.6	3.0	6.0	0.4
⁹⁵ Nb	21,580	58.2	33.7	7.9	0.06
⁹⁹ Mo	121,200	1.2	1.1	97.7	<0.01
^{99m} Tc	17,930	<0.2	0.8	99.2	<0.01
¹⁰³ Ru	4,140	74.0	12.2	12.6	1.2
¹⁰⁶ Ru	1,440	>65	<14	<23	<0.4
¹²⁴ Sb	1,355	60.9	0.8	34.7	3.6
¹²⁵ Sb	344	<54	ND	98.0	2.0
¹⁴⁰ Ba	38,990	14.2	85.8	<0.1	<0.1
¹⁴⁰ La	113,880	63.6	36.3	0.1	<0.1
¹³¹ I	31,980	2.7	2.9	94.0	0.5
¹³³ I	459,200	4.1	<0.05	95.5	0.4
¹³⁷ Cs	16,100	0.1	99.9	<0.1	<0.1
¹⁴⁴ Ce	7,010	~100	<4	<1	<0.06
¹⁵⁴ Eu	670	~100	<3	<40	<0.1

listed, together with the percentages of each radionuclide partitioned between particulate, cationic, anionic and nonionic forms. The relative concentrations of the radionuclides in the incoming trench water vary sporadically, and on January 26, 1983, the most abundant gamma-emitting radionuclides were ^{54}Mn , ^{59}Fe , ^{60}Co , ^{95}Zr , ^{95}Nb , ^{99}Mo , ^{99}Tc , ^{131}I , ^{133}I , ^{137}Cs , ^{140}Ba , ^{144}Ce (see Table 3.1). Also present were smaller amounts of ^{58}Co , ^{103}Ru , ^{106}Ru , ^{124}Sb , ^{125}Sb and ^{154}Eu . The ^{95}Nb , ^{99}Tc and ^{131}I are convenient tracers for the longer-lived isotopes of ^{94}Nb , ^{99}Tc and ^{129}I , respectively, which are of specific interest and listed in 10 CFR 61. Iron-59 is a convenient tracer for the longer-lived ^{55}Fe , which is a major component of power reactor wastes. The ^{60}Co and ^{137}Cs , which are specifically listed in 10 CFR 61, are present in the trench water in concentrations which are appropriate for tracing their localized movement in the groundwater.

Well #1 which is located 30 meters from the trench was sampled on January 27, 1983. The normal suite of mobile radionuclides, e.g., ^{58}Co , ^{60}Co , ^{99}Mo , ^{99}Tc , ^{103}Ru , ^{106}Ru , ^{124}Sb , ^{125}Sb , ^{131}I and ^{133}I were present in the water from Well #1 (see Table 3.2). In addition to these mobile radionuclides, the water from Well #1 contained traces of ^{54}Mn , ^{59}Fe , ^{95}Zr , ^{95}Nb and ^{140}Ba . These radionuclides had never been previously detected at the seepage spring located some 260 meters from the trench. Although traces of ^{137}Cs were observed in soil cores collected from the saturated zone during the drilling of Well #1, the concentration of ^{137}Cs in the water during this sampling period was non-detectable at less than one pCi/l.

At Well #3, located 73 meters from the trench, much lower concentrations of only the mobile suite of radionuclides (^{58}Co , ^{60}Co , ^{103}Ru , ^{106}Ru , ^{125}Sb and ^{131}I) were observed (see Table 3.3). Their extremely low concentrations, plus the absence of the shorter-lived mobile radionuclides ^{99}Mo , ^{99}Tc , ^{124}Sb and ^{133}I , indicates that Well #3 is not located in the mainstream of groundwater movement from the trench. The very low radionuclide concentrations on the soil cores collected during the well drilling tend to confirm this observation.

Table 3.4 lists the radionuclide concentrations and physico-chemical forms in the seepage spring water sampled on January 31, 1983. Since previous measurements of groundwater flow rates between the trench and the springs indicated a travel time of about 4 to 5 days⁽⁵⁾, the seepage springs were sampled 4 days after the trench water sampling, in an attempt to hopefully sample the same parcel of water as it moved from the trench to the springs. The spring water contained the suite of mobile radionuclides normally observed, in concentrations which were intermediate between that observed for Wells #1 and #3.

As the trench water percolates into the soil and flows to the seepage springs, selective removal of the particulate and cationic forms of each radionuclide can be observed. The resulting changes in the predominant chemical species of each radio-

TABLE 3.2. Radionuclide Concentrations and Physicochemical Forms in Water from Well #1 (January, 1983)

WELL #1 (1/27/83 @ 1430)					
RAIONUCLIDE	TOTAL pCi/l	% PARTICULATE	% CATIONIC	% ANIONIC	% NONIONIC
⁵⁴ Mn	90.6	0.08	0.4	99.4	0.1
⁵⁹ Fe	21.6	0.3	16.0	82.2	<1
⁵⁸ Co	12.2	<0.2	8.2	90.2	1.1
⁶⁰ Co	210	0.4	64.8	33.7	1.1
⁹⁵ Zr	19.9	0.09	8.0	90.4	<0.5
⁹⁵ Nb	118	0.08	1.9	97.5	0.3
⁹⁹ Mo	13,590	0.2	0.7	99.0	<0.01
^{99m} Tc	2,400	0.2	<0.8	99.0	<0.01
¹⁰³ Ru	300	0.3	11.7	86.7	1.2
¹⁰⁶ Ru	324	<0.2	10.9	87.6	1.3
¹²⁴ Sb	233	<0.2	0.5	91.0	9.0
¹²⁵ Sb	102	0.2	1.0	83.2	15.6
¹⁴⁰ Ba	40	1.5	<0.1	98.5	<0.1
¹⁴⁰ La	<6	-	-	-	-
¹³¹ I	11,120	0.4	4.9	94.7	<0.1
¹³³ I	21,740	0.5	<0.3	99.2	0.2
¹³⁷ Cs	<1	-	-	-	-
¹⁴⁴ Ce	<60	-	-	-	-
¹⁵⁴ Eu	<50	-	-	-	-

TABLE 3.3. Radionuclide Concentrations and Physicochemical Forms in Water from Well #3 (January, 1983)

WELL #3 (1/26/83 @ 1300)

RADIONUCLIDE	TOTAL pCi/l	% PARTICULATE	% CATIONIC	% ANIONIC	% NONIONIC
⁵⁴ Mn	<1	-	-	-	-
⁵⁹ Fe	<1	-	-	-	-
⁵⁸ Co	0.74	1.0	29.7	58.0	12.3
⁶⁰ Co	165	0.5	63.8	34.2	1.3
⁹⁵ Zr	<1	-	-	-	-
⁹⁵ Nb	<1	-	-	-	-
⁹⁹ Mo	<5	-	-	-	-
^{99m} Tc	<0.2	-	-	-	-
¹⁰³ Ru	14.5	<0.1	8.4	91.1	1.4
¹⁰⁶ Ru	82.6	0.9	9.6	88.3	1.3
¹²⁴ Sb	<1	-	-	-	-
¹²⁵ Sb	22.5	0.4	1.7	96.0	1.8
¹⁴⁰ Ba	<1	-	-	-	-
¹⁴⁰ La	<1	-	-	-	-
¹³¹ I	5.0	<1	<2	>97	<1
¹³³ I	<1	-	-	-	-
¹³⁷ Cs	<1	-	-	-	-
¹⁴⁴ Ce	<1	-	-	-	-
¹⁵⁴ Eu	<5	-	-	-	-

TABLE 3.4. Radionuclide Concentrations and Physicochemical Forms in Spring Water (January, 1983)

SPRINGS (1/31/83 @ 0900)					
RADIONUCLIDE	TOTAL pCi/l	% PARTICULATE	% CATIONIC	% ANIONIC	% NONIONIC
⁵⁴ Mn	<0.1	-	-	-	-
⁵⁹ Fe	<0.2	-	-	-	-
⁵⁸ Co	0.28	<0.3	5.0	92.9	1.7
⁶⁰ Co	62.2	0.2	44.9	50.9	4.0
⁹⁵ Zr	<0.1	-	-	-	-
⁹⁵ Nb	<0.1	-	-	-	-
⁹⁹ Mo	48	<0.2	<12	>88	<0.3
^{99m} Tc	12	<0.1	<1	>99	<0.3
¹⁰³ Ru	39.2	0.1	13.0	83.2	3.6
¹⁰⁶ Ru	45.7	0.3	15.1	80.5	3.9
¹²⁴ Sb	6.2	<0.2	<1.6	26.0	74.2
¹²⁵ Sb	88.0	<0.05	0.6	23.3	76.1
¹⁴⁰ Ba	<0.1	-	-	-	-
¹⁴⁰ La	<0.5	-	-	-	-
¹³¹ I	182	0.4	5.6	92.3	1.5
¹³³ I	7.2	<2	-	100	<8
¹³⁷ Cs	<0.1	-	-	-	-
¹⁴⁴ Ce	<0.4	-	-	-	-
¹⁵⁴ Eu	<0.3	-	-	-	-

nuclide are reflected in the prevalence of the anionic and non-ionic forms of the mobile species down flow from the trench. Figures 3.2 to 3.9 illustrate these changes.

Cesium-137

Cesium-137 is the least mobile of the radionuclides studied to date (see Figure 3.2). In January, 1983, the trench water contained 16,100 pCi/l of ^{137}Cs , essentially all present as a soluble cation. However, the ^{137}Cs was non-detectable in the well and spring water samples. In view of the coarse textures of the soils at this site (see Section 4.0), this was somewhat surprising. Decontamination factors (DF) of $>1.6 \times 10^4$ to $>1.6 \times 10^5$ for the well water and spring water, respectively, were afforded by the soil column. The ten-fold greater DF for ^{137}Cs at the springs is simply due to the fact that a ten-fold larger water sample was taken at the springs. The ^{137}Cs presumably exists in the groundwater as Cs^+ , and the principal retention mechanism on soils is expected to be cation exchange.

Iodine-131

The radioiodine in the trench, well and spring water occurs predominantly in soluble anionic forms (see Figure 3.3). Further studies have shown that about half of the soluble anionic ^{131}I is in the form of iodide (I^-), and the other half apparently occurs as an organically bound anionic complex (see Section 3.3). The ^{131}I is relatively mobile in the groundwater, with DF's of 2.8 and 176 at Well #1 and the springs, respectively. The DF at Well #3 was much higher (6400), again indicating that this well is not situated in the main flow stream from the trench to the springs. The fraction of ^{131}I in the soluble anionic forms does not change appreciably during transport from the trench to the springs. About 3 to 5% of the total ^{131}I is taken up by the cation exchange resin during the sampling. It is not known if this is due to adsorption of a truly cationic species or to reactions of the radioiodine with the organic matrix of the cation resin.

Cobalt-60

The ^{60}Co in the trench water during the January, 1983 sampling was partitioned as follows: 58.5% particulate, 41.3% cationic and 0.1% anionic. As the water moves from the trench to the springs, the selective uptake of the cationic ^{60}Co by the soil is clearly evident, resulting in the anionic ^{60}Co being the predominant form in the spring water (see Figure 3.4). The DF's for the "total" ^{60}Co gradually increased in going from Well #1 to Well #2 to the springs, being 235, 300 and 790, respectively. While the cationic ^{60}Co is reduced in concentration by a factor of 731 in going from the trench water to the springs, the anionic ^{60}Co is reduced by only a factor of 1.5. It appears that the anionic ^{60}Co is one of the most mobile species in this groundwater system. Predictions of chemical forms of cobalt based on

FIGURE 3.2. Change in Physicochemical Forms of ¹³⁷Cs During Migration in Groundwater

FIGURE 3.3. Change in Physicochemical Forms of ^{131}I During Migration in Groundwater

FIGURE 3.4. Change in Physicochemical Forms of ^{60}Co During Migration in Groundwater

thermodynamic data indicate that Co^{+2} would be the predominant solution species with a much smaller contribution from $\text{Co(OH)}^{+}(5)$. A possible form for the anionic ^{60}Co is Co(OH)_3^- , although this ion is predicted to exist at concentrations approximately 8 orders of magnitude lower than Co^{+2} . The discrepancy may be due to organically complexed ^{60}Co which would appear as a soluble anionic form in our separation scheme.

Cobalt-60 has been shown to be one of the few radionuclides to migrate in groundwaters from a variety of other low-level waste disposal sites(6,7,8,9,10). This ubiquitous mobility may be related to the occurrence of the anionic cobalt species.

Ruthenium-103

The ^{103}Ru present in the trench water during the January, 1983 sampling was 74% particulate, 12.2% cationic, 12.6% anionic, and 1.2% nonionic. During migration in the groundwater, the cationic ^{103}Ru was preferentially sorbed to the soil in comparison to the anionic form(s) (see Figure 3.5). Once the ^{103}Ru reached Well #1, the anionic form(s) in the well water accounted for 86.7% of the total ^{103}Ru . The relative amounts of cationic, anionic and nonionic ^{103}Ru did not appreciably change during the ensuing transport to the springs. The overall DF's for Well #1, Well #2 and the springs amounted to 14, 286, and 106, respectively. However, the DF at the springs for the cationic species was 99, whereas the DF for the anionic forms was only 16. The minimal adsorption of the anionic ruthenium species on soils has been previously observed, and based on thermodynamic data, the predicted soluble anionic ^{103}Ru species that would be prevalent in an oxidizing groundwater environment would be $\text{RuO}_4^{-(5)}$.

Antimony-125

The ^{125}Sb in the trench water was present primarily (98%) in a soluble anionic form with 2% being present as a soluble nonionic compound. During migration in the groundwater, the anionic ^{125}Sb was preferentially adsorbed onto the soil compared to the nonionic ^{125}Sb (see Figure 3.6). At the springs the ^{125}Sb was partitioned as follows: 76.1% nonionic, 23.3% anionic, and only 0.6% cationic. The ^{125}Sb is extremely mobile in the groundwater at this site with DF's for "total" Sb species of only 3.4, 15.3 and 3.9 at Well #1, Well #3 and the springs, respectively. Much of the anionic ^{125}Sb appears to be forming in situ in the trench by desorption of the accumulated ^{125}Sb inventory present in the trench sediments, since it's concentration in the groundwater actually increases substantially (7X) as the water moves from the trench to the springs. These experimental observations are in agreement with the predicted chemical forms estimated to be present in oxygenated groundwater, namely the nonionic species HSbO_2^0 and $\text{Sb(OH)}_3^0(5)$.

FIGURE 3.5. Change in Physicochemical Forms of ^{103}Ru During Migration in Groundwater

FIGURE 3.6. Change in Physicochemical Forms of ^{125}Sb During Migration in Groundwater

Niobium-95

Niobium-95 is a convenient tracer in this system for the much longer-lived ^{94}Nb . Niobium-94 is of concern in low-level waste management because it is calculated to be a major constituent in aged neutron activated metal components of reactor pressure vessel internals. Based on the results to date in this groundwater system, the ^{95}Nb does not appear to be very mobile. In the trench water sampled in January, 1983, the ^{95}Nb was partitioned as follows: 58.2% particulate, 33.7% cationic and 7.9% anionic. In water from Well #1, most of the cationic ^{95}Nb had been removed by adsorption on the soil and the anionic ^{95}Nb accounted for 97.5% of the total (see Figure 3.7). During the ensuing movement from Well #1 to the springs, the remaining anionic ^{95}Nb is removed by adsorption on the soil, and ^{95}Nb was not detectable in water from Well #3 and the springs. The DF factors for Wells #1, #3 and the springs amounted to 180, $>2 \times 10^4$, and $>2 \times 10^5$, respectively. No predictions based on thermodynamic data of the chemical species occurring in groundwater have been published.

Iron-59

Iron-59 is a convenient tracer of the longer-lived ^{55}Fe which is one of the most abundant radionuclides in nuclear power plant wastes. The ^{59}Fe is predominantly present in the trench water in a particulate form, and during the January, 1983 sampling the particulate ^{59}Fe accounted for 96.7% of the total (see Figure 3.8). The soluble cationic and anionic species represented 2.3% and 1.0% of the total ^{59}Fe , respectively. Iron-59 has never been detected in the spring water, but a trace of ^{59}Fe was found in Well #1 water partitioned as follows: 82.2% anionic, 16.0% cationic and 0.3% particulate. The anionic ^{59}Fe did not migrate to Well #3 or the springs, and DF's for Well #1, Well #3 and the springs amounted to 2.6×10^3 , $>5.7 \times 10^4$, and $>2.9 \times 10^5$, respectively. Measurements of stable Fe(II) and Fe(III) in the trench waters during the January, 1983 sampling gave concentrations of 6.1 and 84.9 $\mu\text{g}/\text{L}$, respectively. The high concentrations of iron in the trench water are undoubtedly due to corrosion of the steel piping which delivers the effluent water to the trench. It is possible that some of the Fe(III) may be present as colloidal material which passes the 0.4 μ filter used for filtering the water. In Well #1 and the 1/31/83 spring sample, the Fe(II) and Fe(III) concentrations were nondetectable at less than 2 $\mu\text{g}/\text{L}$. Although soluble Fe(II) and Fe(III) were detected in Well #3, the results may be biased by contamination from a pumping system which contained a stainless steel component. During the February sampling the Fe(III) concentrations in the trench waters were 18-19 $\mu\text{g}/\text{L}$. Iron(II) was nondetectable in trench, well and spring waters. Low concentrations of Fe(III) were observed in Well #1 (2 $\mu\text{g}/\text{L}$) and the springs (3 $\mu\text{g}/\text{L}$), and Well #3 contained 15 $\mu\text{g}/\text{L}$.

FIGURE 3.7. Change in Physicochemical Forms of ⁹⁵Nb During Migration in Groundwater

FIGURE 3.8. Change in Physicochemical Forms of ⁵⁹Fe During Migration in Groundwater

Manganese-54

In the trench water the ^{54}Mn occurred as follows: 87.6% cationic, 11.8% particulate and 0.6% anionic (see Figure 3.9). In Well #1 a trace of ^{54}Mn was detected, essentially all in an anionic form. The anionic ^{54}Mn did not migrate to Well #3 or the springs. The DF's for Well #1, Well #3 and the springs amounted to 1.2×10^3 , $>1 \times 10^5$ and $>1 \times 10^6$, respectively. During the February sampling when the relatively high suspended particulate concentrations were present in the trench water, the ^{54}Mn was mainly in a particulate form. Well #1 water contained traces of ^{54}Mn in both particulate and cationic forms, indicating the migration of microparticulates containing ^{54}Mn . Well #3 water contained barely detectable ^{54}Mn , mainly in a particulate form. Manganese-54 was nondetectable in the spring water. The dominant solution species of manganese in this type of water is reported to be Mn^{+2} , with smaller amounts of $\text{Mn}(\text{HCO}_3)^+$ present(13).

Other Radionuclides

A number of other radionuclides of lesser significance in the management of low level wastes are also present in this system. Cobalt-58 is a shorter-lived activation product formed by an (n,p) reaction with stable nickel. Its behavior relative to ^{60}Co , which is formed by an (n, γ) reaction with cobalt, is often slightly different. This may be due to its formation from different parent material, to kinetic differences, and to differences in half-lives which result in a much greater inventory of ^{60}Co in the trench sediments relative to ^{58}Co . If microbial or very slow geochemical processes are affecting the chemical speciation of the radiocobalt then these effects would probably have a more pronounced effect on the longer-lived ^{60}Co .

Zirconium-95 is the precursor of ^{95}Nb and its behavior is somewhat similar. Zirconium-95 is present in the trench water mainly in particulate form, with the anionic form being the dominant soluble species. In Well #1, 90.4% of a trace amount of ^{95}Zr is in an anionic form. The ^{95}Zr has never been detected in the spring water, giving a DF of $>1 \times 10^5$.

Ruthenium-106 exhibits a behavior very similar to that of the shorter-lived ^{103}Ru .

Barium-140 is often present in the trench water and occurs primarily as a cation. A trace of ^{140}Ba was detected in an anionic form in Well #1. It has never been detected at the springs. Its short half-life does not make this an important radionuclide in waste management.

Several rare earth radionuclides, ^{140}La , ^{141}Ce , ^{144}Ce and ^{154}Eu are present in the trench water, mainly in particulate forms. The rare earths could not be detected in well or spring waters, indicating efficient retention by the soil.

^{54}Mn
JAN. 1983

$\text{DF} = 1.2 \times 10^3$

% IN
VARIOUS
FORMS

$\text{DF} > 1 \times 10^5$
ND

$\text{DF} > 1 \times 10^6$
ND

FIGURE 3.9. Change in Physicochemical Forms of ^{54}Mn During Migration in Groundwater

Antimony-124 exhibits behavior very similar to the longer-lived ^{125}Sb in the well and spring water. However, the ^{124}Sb appears to be associated with particulates in the trench water to a greater degree than the ^{125}Sb . This may be due to the fact that the ^{124}Sb is a relatively short-lived neutron activation product and the ^{125}Sb is a longer-lived fission product.

Iodine-133 exhibits behavior very similar to the longer-lived ^{131}I .

February, 1983 Sampling

During the February, 1983 sampling, the trench water was sampled at two locations, its inlet (Manway #1) and at the far end (last Manway) (see Tables 3.5 and 3.6). During the sampling at the inlet it was noticed that the influent trench water contained a relatively high amount of suspended material and an unusually high pH of 9.20. Depending upon the source of the effluent water, the pH may sometimes vary slightly above 9.0, but it is usually in the 7.5-8.5 range.

The observed increase in turbidity was confirmed by the radionuclide analyses which showed the particulate fraction of most radionuclides to also be unusually high. It appears that a low-level discharge of particulate radioactive corrosion products had been released to the trench during the sampling period. The "total" concentrations of most radionuclides at Manway #1 were about twice those observed at the last manway, due to the larger fraction of particulate forms remaining in suspension at the trench inlet (Manway #1). The concentrations of the radionuclides in soluble forms, however, were actually significantly higher at the far end of the trench compared to the inlet end. It is not known if this was due to leaching of the sediment-adsorbed inventory of radionuclides as the water moved through the trench, or whether it merely reflected a temporal variation in the concentrations of radionuclides in the effluent water.

During the February sampling of Well #1 (see Table 3.7), the particulate fraction of many radionuclides increased significantly compared to the January sampling, apparently a reflection of the much greater input of particulate radionuclides into the trench during this period. Apparently, microparticulates can sometimes be transported in the groundwater to Well #1, depending upon their significance in the trench influent water. The anionic forms of ^{54}Mn and ^{59}Fe which had been the dominant soluble species in Well #1 water during the January sampling were of only minor significance during the February sampling. In fact, the cation fraction of most soluble radionuclide species increased during the February sampling. This may be caused by the higher pH of the water during the February sampling compared to the January sampling.

Well #3 water sampled in February again showed lower concentrations than the spring water (see Table 3.8). Also, traces

TABLE 3.5. Radionuclide Concentrations and Physicochemical Forms in Trench Water (February, 1983)

RADIONUCLIDE	TRENCH - MANWAY #1 (2/15/83 @ 1145)				
	TOTAL pCi/l	% PARTICULATE	% CATIONIC	% ANIONIC	% NONIONIC
⁵⁴ Mn	271,800	86.5	12.6	0.8	<0.007
⁵⁹ Fe	496,700	98.9	0.7	0.3	<0.005
⁵⁸ Co	46,800	97.9	2.0	<0.07	<0.02
⁶⁰ Co	473,000	98.1	1.7	0.2	0.07
⁶⁵ Zn	7,220	99.7	0.3	<1	<0.04
⁹⁵ Zr	35,700	90.0	4.3	5.4	0.2
⁹⁵ Nb	102,500	88.2	3.9	7.8	0.1
⁹⁹ Mo	28,950*	-	<1*	100*	<0.01
^{99m} Tc	3,150*	-	<0.4*	100*	<0.03*
¹⁰³ Ru	13,830	88.9	5.6	5.2	0.3
¹⁰⁶ Ru	3,490	>85	<12	<7	0.5
¹²⁴ Sb	10,000	93.0	0.7	5.7	0.8
¹²⁵ Sb	<280	-	-	-	-
¹³¹ I	9,380	-	4.9*	88.6*	0.2*
¹³³ I	13,470*	-	<0.9*	99.4*	0.7*
¹³⁷ Cs	23,000	4.9	96.1	<0.1	<0.01
¹⁴⁰ Ba	14,450*	-	98.6*	1.3	<0.08
¹⁴⁰ La	12,680*	-	96.3	3.7	<0.01
¹⁴¹ Ce	11,100	87.8	12.5	<0.5	<0.02
¹⁴⁴ Ce	11,000	85.9	14.2	<2	<0.05
¹⁵⁴ Eu	590*	-	71*	29*	<3

ND = NON-DETECTABLE

* = SOLUBLE FRACTION ONLY

TABLE 3.6. Radionuclide Concentrations and Physicochemical Forms in Trench Water (February, 1983)

RADIONUCLIDE	TRENCH - LAST MANWAY (2/15/83 @ 1520)				
	TOTAL pCi/l	% PARTICULATE	% CATIONIC	% ANIONIC	% NONIONIC
⁵⁴ Mn	137,500	41.1	58.3	0.6	<0.007
⁵⁹ Fe	250,600	96.6	1.7	1.6	<0.03
⁵⁸ Co	7,060	48.2	51.7	<0.2	<0.05
⁶⁵ Zn	3,390	96.7	3.2	<0.8	<0.008
⁶⁰ Co	214,200	92.0	7.1	0.73	<0.09
⁹⁵ Zr	7,780	39.8	21.2	35.7	3.2
⁹⁵ Nb	24,560	25.0	60.6	14.2	0.2
⁹⁹ Mo	18,900	6.5	0.8	92.7	<0.03
^{99m} Tc	1,970	18.0	<0.6	81.9	<0.04
¹⁰³ Ru	7,660	65.3	21.5	12.4	0.7
¹⁰⁶ Ru	630	100	ND	ND	ND
¹²⁴ Sb	1,760	54.7	2.8	37.6	4.8
¹²⁵ Sb	910	68.7	<8	26.4	4.8
¹³¹ I	7,930	0.8	3.7	95.4	<0.08
¹³³ I	6,660	0.5	<2	99.0	0.5
¹³⁷ Cs	26,640	5.8	94.1	<0.05	<0.008
¹⁴⁰ Ba	31,560	1.0	98.6	0.04	<0.03
¹⁴⁰ La	54,590	11.2	87.5	1.3	<0.08
¹⁴¹ Ce	5,450	57.3	42.7	0.5	0.6
¹⁵⁴ Eu	1,990	94.4	0.9	5.1	<0.5

ND = NON-DETECTABLE

ND = NON-DETECTABLE
TABLE 3.7. Radionuclide Concentrations and Physicochemical Forms in Water from Well #1 (February, 1983)

WELL #1(2/15/83 @ 1430)					
RADIONUCLIDE	TOTAL pCi/l	% PARTICULATE	% CATIONIC	% ANIONIC	% NONIONIC
⁵⁴ Mn	7.88	37.6	60.7	1.8	<5
⁵⁹ Fe	19.5	80.0	17.4	<9	<6
⁵⁸ Co	<2	-	-	-	-
⁶⁰ Co	160	7.8	32.5	57.9	1.4
⁶⁵ Zn	2.7	<11	58.5	40.0	<19
⁹⁵ Zr	1.4	24.3	ND	37.9	<39
⁹⁵ Nb	7.4	9.1	22.2	53.0	4.1
⁹⁹ Mo	1,570	0.5	5.4	94.1	<0.2
^{99m} Tc	127	0.3	5.0	94.5	<0.2
¹⁰³ Ru	316	1.1	21.5	74.7	2.6
¹⁰⁶ Ru	114	1.5	21.0	71.9	6.3
¹²⁴ Sb	203	<0.3	2.1	96.1	1.9
¹²⁵ Sb	188	<0.2	0.5	94.7	5.2
¹³¹ I	1,320	0.8	4.5	94.6	0.08
¹³³ I	129	0.4	12.4	83.7	3.3
¹³⁷ Cs	1.8	27	49	10	15
¹⁴⁰ Ba	<7	-	-	-	-
¹⁴⁰ La	3.9	<15	61	<40	38
¹⁴¹ Ce	<3	-	-	-	-
¹⁵⁴ Eu	5.7	53	ND	48	<14

ND = NON-DETECTABLE

TABLE 3.8. Radionuclide Concentrations and Physicochemical Forms in Water from Well #3 (February, 1983)

WELL #3 (2/17/83 @ 1030)					
RADIONUCLIDE	TOTAL pCi/l	% PARTICULATE	% CATIONIC	% ANIONIC	% NONIONIC
⁵⁴ Mn	1.6	~100	ND	ND	ND
⁵⁹ Fe	3.5	~100	ND	ND	ND
⁵⁸ Co	1.8	<2	57	40	<11
⁶⁰ Co	125	3.0	50	43	3.1
⁶⁵ Zn	3.6	ND	100	ND	ND
⁹⁵ Zr	1.0	33	ND	68	ND
⁹⁵ Nb	<1	-	-	-	-
⁹⁹ Mo	<7	-	-	-	-
^{99m} Tc	<0.5	-	-	-	-
¹⁰³ Ru	13.6	0.9	15	82	3
¹⁰⁶ Ru	66.2	1.8	21.6	76.6	<3
¹²⁴ Sb	<0.5	-	-	-	-
¹²⁵ Sb	21.9	<1	<5	76	24
¹³¹ I	7.2	<1	4	94	<2
¹³³ I	<2	-	-	-	-
¹³⁷ Cs	<1	-	-	-	-
¹⁴⁰ Ba	<3	-	-	-	-
¹⁴⁰ La	<2	-	-	-	-
¹⁴¹ Ce	<0.6	-	-	-	-
¹⁵⁴ Eu	<2	-	-	-	-

ND = NON-DETECTABLE

of particulate ^{54}Mn , ^{59}Fe , ^{60}Co and ^{95}Zr were also observed. Otherwise, the anionic species of the other detectable radionuclides were the dominant forms.

The spring water sampled in February showed essentially the same distribution of physicochemical forms as observed during the January sampling (see Table 3.9). No detectable particulate radionuclides were observed. The anionic species were dominant for all radionuclides except ^{124}Sb and ^{125}Sb , which again appeared predominantly in soluble non-ionic forms.

3.2 Radioiodine Speciation

Iodine-129 (1.59×10^7 yr) has been shown to be one of the most mobile long-lived radionuclides migrating in contaminated groundwaters(7,9), and is therefore of primary concern from a radioactive waste disposal consideration. The ^{131}I present in the trench/springs system can serve as a useful analog for the ^{129}I which is difficult to measure and is present in much lower concentrations compared to the ^{131}I . The environmental behavior and mobility of radioiodine is strongly influenced by its chemical forms. Therefore, the behavior of radioiodines (specifically, their adsorption on soils) in the soil-water system of the trench and springs should be a reflection of the chemical forms in which the iodine occurs.

All previous studies of the dissolved forms of radioiodine at the trench/springs system indicated that the radioiodine was predominantly in a form which was removed from solution by anion exchange resin. However, the ionic form studies using anion and cation exchange resins are not capable of discerning between I^- , IO_3^- or possibly other anionic species.

At neutral or slightly basic pH's, the I^- and IO_3^- species are reported to be able to coexist as stable ions in aqueous solutions(11). There is a possibility, however, that some fraction of the ^{131}I that is retained on the anion exchange resin may be in some other anionic form. Behrens(12) has shown that a portion of the I^- present in river water can be converted by microbial processes into several unidentified anionic species, presumably organic iodine compounds.

Therefore, a technique was developed to partition the radioiodine into the two major inorganic species (I^- and IO_3^-) and organically bound iodine suspected to be present in the trench water and groundwater. This method is based on the different anion exchange behavior of I^- and IO_3^- on Dowex-1 anion exchange resin. The I^- is quantitatively retained on anion exchange resin while IO_3^- is not. The organically bound iodine is separated from the I^- by quantitatively coprecipitating the I^- on fresh AgCl , while the IO_3^- and organically bound iodine remain in solution. By combining these methods, it is possible to differentiate between I^- , IO_3^- and organically bound iodine in the trench and groundwaters.

TABLE 3.9. Radionuclide Concentrations and Physicochemical Forms in Spring Water (February, 1983)

SPRINGS (2/18/83 @ 1330)

RADIONUCLIDE	TOTAL pCi/l	% PARTICULATE	% CATIONIC	% ANIONIC	% NONIONIC
⁵⁴ Mn	<0.07	-	-	-	-
⁵⁹ Fe	<0.2	-	-	-	-
⁵⁸ Co	0.35	<0.1	10	89	<2
⁶⁰ Co	43	<0.07	26	67	7
⁶⁵ Zn	<0.2	-	-	-	-
⁹⁵ Zr	<0.1	-	-	-	-
⁹⁵ Nb	<0.1	-	-	-	-
⁹⁹ Mo	29.6	ND	ND	~100	ND
^{99m} Tc	3.6	ND	ND	~100	ND
¹⁰³ Ru	33	<0.03	3	92	5
¹⁰⁶ Ru	32	<0.2	4	88	7
¹²⁴ Sb	5.0	ND	ND	ND	100
¹²⁵ Sb	63	<0.008	2	<0.2	98
¹³¹ I	341	<0.02	<0.7	91	8
¹³³ I	0.23	ND	ND	~100	ND
¹³⁷ Cs	<0.03	-	-	-	-
¹⁴⁰ Ba	<0.3	-	-	-	-
¹⁴⁰ La	<0.03	-	-	-	-
¹⁴¹ Ce	<0.1	-	-	-	-
¹⁵⁴ Eu	<0.3	-	-	-	-

ND = NON-DETECTABLE

The following procedure was developed for identifying these forms. Dowex 1x8, 50-100 mesh anion exchange resin was prepared in columns 2.5 cm diameter by 2.5 cm high. One liter aliquots of trench and groundwater were adjusted to pH 10 with dilute NaOH. The samples were then passed through the resin columns at a flow rate of 20 ml/min. Utilizing $^{131}\text{I}^-$ and $^{131}\text{IO}_3^-$ tracers, it was found that under these conditions, $99.7 \pm 0.3\%$ of the $^{131}\text{I}^-$ (and presumably organically bound iodine anions) are retained on the resin, while $75.1 \pm 1.9\%$ of the $^{131}\text{IO}_3^-$ passes through the resin. Separate 2 liter aliquots of trench and groundwater were used for the AgCl coprecipitation of I^- by adding 25 ml of 2N NaCl, 40 ml of 1N AgNO_3 and 50 ml of 2N MgSO_4 (to aid coagulation of the AgCl) while stirring vigorously. The samples were allowed to stand overnight and the AgCl was then removed by filtration. Under these conditions greater than 94% of the I^- is coprecipitated, as previously determined using $^{131}\text{I}^-$ tracers. The AgCl precipitate and the supernate from the trench and groundwater samples were then counted to measure the ^{131}I in each fraction. The I^- , IO_3^- and organic iodine species were then computed from the following relationships:

$$\text{I}^- = \frac{\text{coprecipitated I}}{0.94 \text{ (yield factor)}}$$

$$\text{IO}_3^- = \frac{\text{effluent through resin column}}{0.751 \text{ (yield factor)}}$$

$$\text{Organic I} = (\text{nonprecipitable I}) - (\text{IO}_3^-)$$

Samples of trench water, Well #1 water and seepage spring water collected in January, 1983 were analyzed by this method and gave the following results.

TABLE 3.10. Chemical Speciation of Radioiodine in Trench, Well and Spring Waters

Sample	Date	Chemical Forms of ^{131}I	% of Total
Trench water	1/26/83	I^-	48
		IO_3^-	3
		Organic I	49
Well #1 water	1/27/83	I^-	46
		IO_3^-	2
		Organic	52
Spring water	1/31/83	I^-	42
		IO_3^-	1
		Organic	57

It is apparent that approximately half of the total ^{131}I in the trench, well and spring waters is in a form which is presumed to be organically bound, with almost equal amounts occurring as I^- . The iodate (IO_3^-) fraction amounted to only a few percent of the total ^{131}I . The organically bound ^{131}I appeared to slightly increase in concentration and the I^- form appeared to slightly decrease as the water moved from the trench to the springs. Microbial conversion of the I^- to organically bound iodine may possibly be occurring in this system and could account for the observed partitioning of the various chemical forms. The warm water and decaying vegetable matter in the trench would provide an ideal environment for microbial mediated processes to occur. Studies are being planned for FY 1983-84 to identify the actual chemical form of the organically bound ^{131}I and to determine its behavior in groundwater relative to I^- , the major inorganic form.

3.3 Physicochemical Speciation of ^{63}Ni in Trench and Spring Waters

The physicochemical speciation and behavior of ^{63}Ni in this groundwater system is of special interest because of its listing in 10 CFR 61 as a radionuclide of primary concern in low-level waste management. This concern is based on the long half-life of ^{63}Ni (100 yr.) and the fact that it is an abundant radionuclide in nuclear power plant low-level wastes.

Therefore, a suite of water and soil samples collected in June, 1981, were analyzed for ^{63}Ni to determine its concentrations and physicochemical forms. Water from the trench and the springs was sampled using the system described in Section 3.0, which partitions the radionuclides into particulate, cation, anionic and nonionic forms. The ^{63}Ni taken up on the filters, resins and Al_2O_3 was leached with hot concentrated HCl , radiochemically separated, electro-deposited on stainless steel discs, and counted in a specially constructed, anticoincidence shielded, low-level beta proportional counter.

The results of these analyses are shown in Table 3.11.

TABLE 3.11. Nickel-63 Concentrations and Chemical Speciation, June, 1981

	<u>Trench Water</u> <u>pCi/l</u>	<u>% of Total</u>
Particulate	199.6 $\pm$ 28	59.1
Cationic	107.4 $\pm$ 38.4	31.8
Anionic	16 $\pm$ 16	4.7
Nonionic	15 $\pm$ 15	4.4
	<u>Spring Water</u> <u>pCi/l</u>	
Cationic	<0.8	
Anionic	<1.9	
Nonionic	1.2 $\pm$ 0.2	

	<u>Trench Sediment</u> <u>pCi/gram</u>
Sediment #2	$3.32 \pm 0.04 \times 10^5$
Sediment #4	$6.42 \pm 0.09 \times 10^4$
	<u>Spring Soil</u> <u>pCi/gram</u>
Soil	18.7 ± 6.6

The ^{63}Ni concentrations in the trench water and sediments are readily measurable. The ^{63}Ni in the water was partitioned as follows: 59.1% particulate, 31.8% cationic, 4.7% anionic and 4.4% nonionic. The cationic and anionic forms were nondetectable in the spring water, but a significant fraction appeared to be in a nonionic form which was retained on the activated Al_2O_3 .

Trench sediments collected near the inlet (Sediment #2) and midway down the trench (Sediment #4) contained ^{63}Ni concentrations of 3.32×10^5 and 6.42×10^4 pCi/gram, respectively. A sieved sample of soil from the spring contained 18.7 ± 6.6 pCi/gram of ^{63}Ni , indicating that traces of ^{63}Ni have migrated to the springs.

This cursory examination of the occurrence of ^{63}Ni in this system indicates that the concentrations are high enough to permit more thorough and detailed studies of its behavior during migration from the trench to the springs.

3.4 Groundwater Chemical Analyses

Samples for complete chemical analyses of the trench, wells, and spring waters were collected at the time of sampling for the radionuclides. All of the anions, cations, trace elements and parameters having a potential role in controlling the chemical speciation of the radionuclides were included in the analyses, (see Tables 3.12 and 3.13). Temperature, pH, Eh, dissolved oxygen and alkalinity were measured onsite during the sampling process. Aliquots of 0.4 μ filtered water were preserved by freezing for laboratory analyses of major anions by ion chromatography. For major cation and trace element analyses, a separate aliquot of filtered water was acidified by adding 20 ml of concentrated Ultrex® hydrochloric acid per liter of water. For the sulfide analyses, an inline filtered sample of water was collected in a glass bottle containing a sufficient quantity of an antioxidant preservative solution. Sulfide analyses were performed by a very sensitive polarographic technique. Another aliquot of filtered water was also collected and preserved by refrigeration for dissolved organic constituent analyses. The details of the procedures for the organic analyses are given in Section 5.

The trench, well and spring waters are generally well oxygenated as evidenced from the dissolved oxygen and Eh measurements. The pH of the trench water is somewhat influenced by operating con-

TABLE 3.12. Chemical Composition of Trench,
Well and Spring Waters

Constituent	Trench 1/26/83	Well #1 1/27/83	Well #3 1/26/83	Spring 1/28/83	Spring 1/31/83
Temp. °C	21	18	18	20	20
pH	7.30	8.10	8.15	8.10	8.15
Eh (mv)	+405	+430	+355	+435	+385
Dissolved O ₂ (mg/l)	6.9	7.2	9.2	4.9	4.5
Alkalinity (HCO ₃ ⁻ -mg/l)	38.0	54.9	52.8	57.5	57.7
DOC (mg/l)	<1	<1	<1	<1	<1
Ca (mg/l)	16.3	25.2	25.3	26.0	20.1
Mg (mg/l)	4.0	4.2	4.2	4.3	4.8
Na (mg/l)	1.68	1.70	1.70	1.99	2.17
K (mg/l)	0.40	1.0	1.0	0.50	1.8
Sr (mg/l)	0.081	0.093	0.093	0.094	0.12
SO ₄ ⁻² (mg/l)	14.3	13.9	12.2	13.5	13.9
S ⁼ (polarographic) (mg/l)	<0.003	<0.003	<0.003	<0.003	<0.003
S (total by ICP) (mg/l)	5.6	5.1	5.1	5.4	4.6
NO ₃ ⁻ (mg/l)	9.2	13.2	8.2	12.5	13.2
NO ₂ ⁻ (mg/l)	2.5	<0.05	<0.05	<0.05	<0.05
F ⁻ (mg/l)	<0.15	<0.15	<0.15	<0.15	<0.15
PO ₄ ⁻³ (mg/l)	3.8	<0.2	<0.2	<0.2	<0.2
P (total by ICP) (mg/l)	1.48	<0.1	<0.1	<0.1	<0.1
Cl ⁻ (mg/l)	0.90	0.87	0.70	0.83	0.87
Si (mg/l)	1.8	4.4	4.4	2.9	8.2
Al (μg/l)	<50	<50	<50	<50	<50
As (μg/l)	<30	<30	<30	<30	<30
B (μg/l)	10	10	10	10	10
Ba (μg/l)	34	28	26	16	14
Co (μg/l)	<10	<10	<10	<10	<10
Cr (μg/l)	<10	<10	<10	<10	<10
Fe (total by ICP) (μg/l)	110	<20	<20	<20	<20
Fe ⁺² (colorimetric) (μg/l)	6.1	<2*	6.1*	3.6	<2
Fe ⁺³ (colorimetric) (μg/l)	84.9	<2*	5.9*	2.5	<2
Fe ⁺² /Fe ⁺³	0.067	-	1.03	1.44	-
Li (μg/l)	<5	<5	<5	<5	<5
Mn (μg/l)	<10	<10	<10	<10	<10
Mo (μg/l)	<10	<10	<10	<10	<10

TABLE 3.12. Chemical Composition of Trench, Well and Spring Waters (continued)

Constituent	Trench	Well #1	Well #3	Spring	Spring
Ni ($\mu\text{g}/\text{l}$)	<20	<20	<20	<20	<20
Se ($\mu\text{g}/\text{l}$)	<100	<100	<100	<100	<100
Ti ($\mu\text{g}/\text{l}$)	<10	<10	<10	<10	<10
V ($\mu\text{g}/\text{l}$)	<5	<5	<5	<5	<5
Zn ($\mu\text{g}/\text{l}$)	24	<10	<10	<10	<10

*Water pumped through stainless steel sampling device - probable contamination with iron.

TABLE 3.13. Chemical Composition of Trench, Well and Spring Waters

Constituent	Trench (1st Manway 2/15/83)	Trench (Last Manway) 2/15/83	Well #1 2/15/83	Well #3 2/17/83	Springs 2/17/83
Temp. °C	17	15	15	19	21
pH	9.20	9.25	8.15	8.40	8.10
Eh (mv)	+155	+150		+350	+340
Dissolved O ₂ (mg/L)	6.58	5.91	5.57	6.64	5.14
Alkalinity (HCO ₃ ⁻ -mg/L)	63.3	63.0	65.5	53.7	57.1
DOC (mg/L)	0.4	0.7	0.4	2.3	0.3
Ca (mg/L)	15.5	16	23	21	26
Mg (mg/L)	3.9	4.0	4.0	4.9	4.4
Na (mg/L)	1.63	1.72	2.11	2.23	1.82
K (mg/L)	0.4	0.4	0.4	1.2	0.8
Sr (mg/L)	0.082	0.083	0.089	0.1	0.09
SO ₄ ⁻² (mg/L)	10.0	6.7	14.6	8.8	12.5
S ⁼ (polarographic)(mg/L)	<1 x 10 ⁻⁵	<1 x 10 ⁻⁵	<1 x 10 ⁻⁵	<1 x 10 ⁻⁵	2 x 10 ⁻
S (total by ICP)(mg/L)	6.2	6.4	7.6	4.7	6.0
NO ₃ ⁻ (mg/L)	1.3	1.3	16.3	8.0	13.5
NO ₂ ⁻ (mg/L)	3.4	1.7	<0.03	<0.03	<0.03
F ⁻ (mg/L)	<0.08	<0.08	<0.08	<0.08	<0.08
PO ₄ ⁻³ (mg/L)	<0.2	<0.2	<0.2	<0.2	<0.2
P (total by ICP)(mg/L)	<0.1	<0.1	<0.1	<0.1	0.18
Cl ⁻ (mg/L)	0.59	0.40	0.97	0.55	0.86
Si (mg/L)	1.74	1.80	2.88	8.50	4.50
Al (µg/L)	<30	100	<30	70	100
As (µg/L)	<20	<20	<20	<20	<20
B (µg/L)	20	20	10	20	20
Ba (µg/L)	30	31	14	16	30
Cr (µg/L)	<10	<10	<10	<10	<10
Fe (total by ICP)(µg/L)	30	30	<5	20	10
Fe ⁺² (colorimetric)(µg/L)	<2	<2	<2	<2	<2
Fe ⁺³ (colorimetric)(µg/L)	19	18	2	15	3
Li (µg/L)	<5	<5	<5	<5	<5
Mn (µg/L)	<3	<3	<3	<3	<3
Mo (µg/L)	<10	<10	<10	<10	<10
Ni (µg/L)	<20	20	<20	20	20
Se (µg/L)	<100	<100	<100	<100	<100
Ti (µg/L)	<5	<5	<5	<5	<5
V (µg/L)	<5	<5	<5	8	13
Zn (µg/L)	37	11	<5	<5	<5

ditions at the source of the effluent water, and ranged from 7.30 on January 26, 1983 to 9.25 on February 15, 1983. The pH of the well and spring waters ranged from 8.1 to 8.4 during both sampling periods. The inorganic constituents are dominated by the anions HCO_3^- , SO_4^{2-} and NO_3^- , and the cations Ca, Mg and Na. The dissolved organic carbon (DOC) content has always been observed to be very low, and in January and February the concentrations were below 1 ppm. Sulfide measurements were below the limits of detection, which were $<3 \mu\text{g}/\text{L}$ in January and $<0.01 \mu\text{g}/\text{L}$ in February. The lower detection limit for the February samples was the result of a reduced procedural blank.

Lower concentrations of nitrite ion (NO_2^-) were observed in the trench waters on both sampling dates, but were never detected in the well and spring waters.

Total iron concentrations determined by ICP analysis in the trench water sampled in January were very high ($100 \mu\text{g}/\text{L}$). Using a colorimetric method (ferrozine) to determine oxidation states, it was found that most of this iron was present as Fe(III). Since this concentration exceeds the solubility product of $\text{Fe}(\text{OH})_3$, this iron is suspected to be either colloidal or chelated iron. The total iron measured by ICP analysis in the trench water sampled in February was lower ($30 \mu\text{g}/\text{L}$), and again was shown to be primarily Fe(III). The iron concentrations in the well and spring waters were much lower than at the trench. Detectable Fe (III) was observed in Well #3 water on both sampling dates and in the spring water during the January sampling. However, the well water sampling during the January sampling of Well #3 utilized a pumping system that contained some stainless steel components which could have contributed to iron contamination.

4.0 Soil Textures and Mineralogy

The aqueous low-level waste disposal site is located in glacial outwash gravels. The glacial outwash gravels average approximately 6 meters in thickness in the vicinity of the disposal site. Boulders of from 25 to 50 cm are common, and the upper 0.6 meter of gravel deposits contain much silt and sand which appear to have been deposited as the glacial meltwater velocity and volume decreased. Eolian material deposited on the surface and carried down into the outwash gravels may also account for part of the silt and sand near the surface. The unsorted glacial outwash gravels overlay approximately 26 meters of gravels and a mixture of sand and gravel. These sands and gravels are unconsolidated in most areas, but locally they may be cemented by calcium carbonate and iron oxides. The gravels and cobbles were deposited with silts, sand, and some clay. The gravels and sand and gravel mixtures exhibit deltaic bedding which is characteristic of these deposits. The sand and gravels are underlaid by clay which is considered to be the bottom of the unconfined aquifer in this area.

Three soil samples collected from an exposed cutaway bank between the trench and the springs were analyzed for grain size. The results are shown in Table 4.1.

A photograph showing the typical strata at this site is shown in Figure 4.1. The sand, silt and clay fractions can be seen in the interstitial material packed in between the cobbles and boulders.

A cursory mineralogical analysis of these soils by x-ray diffraction, plus soils from the saturated zones in Wells #1, #2, #3 and the seepage springs, showed that the major minerals associated with these deposits were quartz and various feldspars. These two minerals accounted for roughly 80% of the total material. The clay minerals were composed of kaolinite, montmorillonite and illite, with the kaolinite being dominant. Other trace minerals identified in the x-ray diffraction patterns included calcite, biotite and amphibole which accounted for no more than a few percent.

TABLE 4.1. Grain Size Analysis of Soils Sampled from a Cutaway Soil Bank Between the Trench and Springs

<u>Soil No.</u>	<u>Grain Size</u>	<u>Weight %</u>
1	>2 mm	78.3
	sand	18.9
	silt	2.2
	clay	0.6
2	>2 mm	77.4
	sand	21.6
	silt	0.3
	clay	0.7
3	>2 mm	80.8
	sand	17.3
	silt	1.2
	clay	0.7

5.0 Characterization of Organic Matter in Trench Sediments

Because organic constituents may play an important role in the mobilization of radionuclides in groundwaters, an extensive analysis of the organic matter extracted from trench sediments was conducted. The objective of this work was to seek to identify possible organic compounds which could form complexes with the various radionuclides present in the trench sediments, and thus enhance their mobility.

5.1 Sample Collection and Preparation

Sediment samples were collected at three different locations along the trench (Manways 2, 6, and 9) on June 7, 1982, using a teflon beaker attached to a long pole (see Figure 5.1). Each sample was placed in an acid-cleaned glass bottle and taken to the lab immediately, where they were stored at 4°C.

FIGURE 4.1. Photograph of a Cutaway Soil Bank Near the Study Area Showing Interstitial Sand, Silt and Clay Interspersed Between Cobbles and Boulders

FIGURE 5.1. Sediment Sampling Locations in the Trench

The analytical procedure used on the sediments is outlined in Figure 5.2. Each sediment sample (~25 gms) was dried on a hot plate under N₂. Two subsamples of each sediment (~10 gms each) were separated for the organic analyses. The remaining sediment was set aside for radionuclide analysis. Twenty mls of milli-Q-purified water (pH 8) were added to each of the two subsamples followed by 5 min of sonication and 10 min of magnetic stirring. After centrifugation, the aqueous extract was decanted and set aside for further analysis of the hydrophilic organics. The once-extracted sediment was redried and set aside for further extraction of the hydrophobic organics.

The aqueous extract was extracted three times with equal volumes of chloroform to remove any nonpolar organics which might interfere with the analysis of the hydrophilic organics in the aqueous extract. The chloroform extract was concentrated and set aside for gas chromatography (GC) and GC-mass spectrometry (GC-MS) analyses of any organics present in this fraction. The purified aqueous extract was subsequently evaporated to dryness under N₂. The residue of this extract was then methylated in a sealed vial with 1 ml of BF₃/methanol at 100°C for 40 min. After cooling, 1 ml of chloroform was added, the mixture was transferred to a test tube containing 3 ml of 1M KH₂PO₄ buffer solution (pH 7) and vortexed. Part of the chloroform layer (0.5 ml), which contained the methylated hydrophilic organics, was then evaporated under nitrogen. The residue was redissolved in chloroform and analyzed for organics by GC and by GC-MS.

The once-extracted sediment was redried and thrice extracted with a mixture of toluene:methanol (3:1 V/V). Twenty mls of the solvent mixture were added to each subsample of the once-extracted sediment followed by 5 min of sonication and 10 min of magnetic stirring. After centrifugation, the hydrophobic organic extract was decanted, concentrated and set aside for GC and GC-MS analyses. The twice-extracted sediment was redried and set aside for radionuclide analyses.

5.2 GC and GC/MS Analyses

GC analyses were performed on a Hewlett-Packard 5880 gas chromatograph equipped with a 60 m x 0.25 mm I.D. fused silica capillary column coated with a 0.25 µm film of SE-52. From an initial value of 40°C, the column temperature was programmed at 20°C per minute for three minutes to 100°C followed by 8°C per minute for 25 minutes to 300°C, and finally maintained isothermally at 300°C for 10 minutes.

GC-MS analyses were performed on a Hewlett Packard 5985 GC-MS instrument in the electron-impact (70-eV) mode. The gas chromatograph on the 5985 instrument was equipped with a 60 m x 0.25 mm I.D. fused silica capillary column coated with 0.25 µm of SE-54; the column was programmed from 40°C to 300°C at 5°C/min, where it was maintained isothermally for 8 min. A splitless injection system was used to introduce the sample onto the GC-MS instrument. A mass range of 50 to 400 amu was scanned every 1.0 sec by computer (HP-2100MX equipped with the HP-7920 Large Disc Drive).

FIGURE 5.2. Analysis Scheme for the Extraction and Analysis of Organics and Radionuclides from Trench Sediments

The organic species identified by the GC-MS analyses were quantitated by GC analysis using internal and external standardization methods. Pure compounds representative of the various compound classes identified by GC-MS were selected as standards and methylated. A specific amount of each standard was co-injected with each sample to confirm the GC-MS identifications. For quantitation purposes, each standard was injected onto the gas chromatograph prior to and following sample analyses. The response factor of each standard was calculated under analytical conditions identical to those of the sample analyses.

5.3 Organic Constituents in Trench Sediments

Organic Extracts

The relative amounts (percent dry weights) of the various organic extracts of the trench sediments are plotted in Figure 5.3. The nonpolar extract contained very little residue. The hydrophilic organic fraction, derived from the purified aqueous extract, contained appreciable amounts of residue, particularly in Manway 6, where it constituted 46% of the total extracted residues. The hydrophobic organic extract was the most abundant of the various extracts, particularly in Manways 2 and 9 where it accounted for 63% and 68%, respectively, of the total extracted residues. In Manway 6, the relative abundance of the hydrophobic organic fraction was lower, whereas the contribution by the hydrophilic organic fraction was enhanced.

Hydrophilic Organics

A variety of carboxylic acids were identified in the hydrophilic organic fraction of the trench sediments (Table 5.1), generally at ppb levels. The soil from Manway 6 was much richer in total acids (9609 ppb) compared to Manways 2 (482 ppb) and 9 (1630 ppb). Several classes of carboxylic acids are represented: tricarboxylic acids, dicarboxylic acids, monocarboxylic acids, oxygenated acids and aromatic acids (see Figure 5.4).

The least abundant of the carboxylic acids identified in the trench sediments are the tricarboxylic acids. Citric acid is the only species identified in this class. It was present in the sediments from Manways 2 and 6 at concentrations of 34 ppb and 159 ppb, respectively. Citric acid constitutes only 7% and 2% of the total carboxylic acids in Manways 2 and 6, respectively. In contrast, as reported earlier, citric acid was the major hydrophilic organic species (380 ppb) in a sample of the effluent water entering the trench (collected on 9/22/81). The latest data indicate that citric acid is not accumulating in the trench sediments. A likely explanation is that citric acid is being metabolized by the trench's microbiota; since it is a common metabolic intermediate and is easily digested by bacteria.

The dicarboxylic acids are the most abundant class of acids identified in the trench sediments; 44% of the total acids in Manway 2; 73% in Manway 6; and 68% in Manway 9. In Manway 2, two of these

FIGURE 5.3. Organic Extracts of Trench Sediments (See Figure 2 for the origin of the extracts.)

TABLE 5.1. Hydrophilic Organics in Trench Sediments

	CONCENTRATION (ppb) ^c IN DRIED SEDIMENT FROM MANWAYS		
	NO. 2	NO. 6	NO. 9
TRICARBOXYLIC ACIDS			
CITRIC ACID ^d	34	159	
DICARBOXYLIC ACIDS			
OXALIC ACID ^d	13	1971	347
MALONIC ACID ^d	8	903	141
MALEIC ACID ^d	3	375	31
SUCCINIC ACID ^d	33	1992	328
2-METHYL-SUCCINIC ACID ^d		94	
PENTANEDIOIC ACID ^d		282	
HEXANEDIOIC ACID ^d	3	193	34
HEPTANEDIOIC ACID ^d	20		
OCTANEDIOIC ACID ^d	41	592	67
NONANEDIOIC ACID ^d	91	587	163
CARBOXYLIC ACIDS			
TETRADECANOIC ACID ^d	3	65	34
HEXADECANOIC ACID ^d	49	292	55
OCTADECANOIC ACID ^d	45	190	39
OXYGENATED ACIDS			
2-HYDROXY-PROPANOIC ACID ^d		138	
3-HYDROXY-BUTANOIC ACID ^d	12		
4-METHOXY-BUTANOIC ACID ^d		16	
2-METHOXY-2-BUTENOIC ACID ^d	49		
4,4-DIMETHOXY-2-PENTENEDIOIC ACID ^d	21		
2-METHOXY-BENZOIC ACID ^d		274	80
2-OXO-PROPANOIC ACID ^d		10	3
4-OXO-PENTANOIC ACID ^d	2	169	39
AROMATICS			
BENZENEACETIC ACID ^d		222	79
FURANCARBOXYLIC ACID ^d		120	20
BENZOIC ACID ^d		362	45
DIMETHYL PHTHALATE	34	188	68
DIBUTYL PHTHALATE	21		
BENZALDEHYDE		96	14
2,6-PYRIDINECARBOXYLIC ACID ^d	92		
PYRIDINECARBOXYLIC ACID ^d		4	
NITROBENZOIC ACID ^{d,e}		115	
NITRO-HYDROXYBENZOIC ACID ^{d,e}		300	57

a) METHYLATED, BF₃/METHANOL;

b) SAMPLED ON 6/7/82;

c) NO ENTRY INDICATES COMPOUND IS BELOW DETECTION LEVELS;

d) METHYL ESTER;

e) TENTATIVE IDENTIFICATION

FIGURE 5.4. Classes of Carboxylic Acids Identified in the Hydrophilic Organic Fraction from the Trench Sediments (See Figure 2 for the origin of the organic fraction.)

species, oxalic and succinic acids, were present at ppm levels (1.97 ppm and 1.99 ppm, respectively). Some of the dicarboxylic acids are common metabolic intermediates in microbiota. Such acids are also formed by some bacteria via oxidation of monocarboxylic acids or alkanes, e.g. ω -oxidation of monocarboxylic acids (fatty acids).

The monocarboxylic acids identified in the trench sediments are considerably less abundant than the dicarboxylic acids: 20% of the total acids in Manway 2, 6% in Manway 6, and 8% in Manway 9. Of these species palmitic acid (hexadecanoic acid) was most abundant followed by stearic acid (octadecanoic acid). In an earlier analysis of spring water (collected on 9/22/81), palmitic and stearic acids were the major hydrophilic organic components, but at much lower levels (1.8 ppb and 2.3 ppb, respectively). Monocarboxylic acids, or fatty acids, such as palmitic and stearic acids are common metabolic intermediates and structural components of microbiota. They are also present in detergents, and this could be another source of these compounds.

The oxygenated carboxylic acids identified in one trench sediment include hydroxy-, methoxy- and oxo-substituted acids. The concentrations of oxygenated acids are comparable to those of the monocarboxylic acids: 17% of the total acids in Manway 2 (vs. 20% for the monocarboxylic acids), 6% in Manway 6 (vs. 6%) and 7% in Manway 9 (vs. 8%). A probable source of these compounds is bacterial diagenesis of unoxygenated carboxylic acids and/or alkanes. Some bacteria, for example, oxidize alkanes to hydroxy-monocarboxylic acids.

Unlike the other classes of carboxylic acids, the concentrations of the aromatic acids in the sediments from the three Manways were roughly comparable: 11% of the total acids in Manway 2, 14% in Manway 6, and 17% in Manway 9. Perhaps the two compounds of most interest are the two nitro-substituted benzoic acids we have tentatively identified, nitrobenzoic acid and nitro-hydroxybenzoic acid. The fragmentation patterns of the two species from the GC-MS analysis strongly suggest these two structures, but we are looking at the evidence more closely to confirm their identities.

Elemental sulfur also appeared in the hydrophilic organic fraction of the sediments. It was not included in Table 5.1 because it is not a hydrophilic organic compound. Based on the GC-MS analyses, sulfur was most abundant in the sediment from Manway 2 (see Figure 5.5). The concentration of sulfur then dropped off exponentially in the sediments from Manways 6 and 9. Absolute concentrations for the sulfur have not been reported because its GC-MS response factor was not determined, and the analytical procedure developed for the trench sediments was not designed for quantitative extraction of sulfur. Previous studies indicate that the concentrations of elemental sulfur in effluent water entering the trench are not high enough to explain the amount of sulfur in Manway 2. The origin of the elemental sulfur is unknown at the present time.

FIGURE 5.5. Elemental Sulfur in the Aqueous Extract of the Trench Sediments

Nonpolar Organics:

The nonpolar organic compounds extracted from the trench sediments did not constitute a significant fraction of the total organics. Trace levels of a few alkanes and alkenes were barely detectable. This is not particularly surprising in that the nonpolar organic fraction is a chloroform extract of the aqueous extract of the trench sediment. This extraction was included in the analytical procedure mainly as a back-extraction to purify the aqueous extract, thereby facilitating the analysis of the hydrophilic organics, which may mediate radionuclide migration in groundwater.

Hydrophobic Organics

The organic content of the hydrophobic organic extract was easily the most complex of the extracts analyzed. The hydrophobic organic extract accounted for much of the total organic extracts of the sediments, specifically 52-68%. It was too complex to permit thorough GC and GC-MS analyses. Many of the organic species in this extract may actually be so nonvolatile that they are unchromatographable by GC and GC-MS. More chromatographic fractionation will be necessary before the hydrophobic organics can be exhaustively characterized. Nevertheless, some species could be identified. Alkanes, alkenes, alkynes and elemental sulfur were identified in the hydrophobic organic extracts from all three trench sediments. The most notable observation about the hydrophobic organic extract, however, is that three cyclic sulfur species were identified in the extract from Manway 2: a five-membered ring compound, CH_2S_4 ; a six-membered ring compound, CH_2S_5 ; and a seven-membered ring compound, CH_2S_6 (see Figure 5.6). We are currently assessing whether or not such species can mediate radionuclide transport in soils.

FIGURE 5.6. Sulfur Species Identified in the Trench Sediments from Manway 2

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NRC FORM 335 <small>(11-81)</small>		U.S. NUCLEAR REGULATORY COMMISSION BIBLIOGRAPHIC DATA SHEET		1. REPORT NUMBER (Assigned by DDC) NUREG/CR-3554 PNL-4773	
4. TITLE AND SUBTITLE (Add Volume No., if appropriate) Radionuclide Migration in Groundwater Annual Progress Report for 1982				2. (Leave blank)	
				3. RECIPIENT'S ACCESSION NO.	
7. AUTHOR(S) D. E. Robertson, A. P. Toste, K. H. Abel and R. L. Brodzinski				5. DATE REPORT COMPLETED MONTH November YEAR 1983	
9. PERFORMING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code) Pacific Northwest Laboratory P.O. Box 999 Richland, WA 99352				DATE REPORT ISSUED MONTH January YEAR 1984	
				6. (Leave blank)	
				8. (Leave blank)	
12. SPONSORING ORGANIZATION NAME AND MAILING ADDRESS (Include Zip Code) Division of Health, Siting, and Waste Management Office of Nuclear Regulatory Research U. S. Nuclear Regulatory Commission Washington, D. C. 20555				10. PROJECT/TASK/WORK UNIT NO.	
				11. FIN NO. B-2380	
13. TYPE OF REPORT Annual Progress Report			PERIOD COVERED (Inclusive dates) FY 1982		
15. SUPPLEMENTARY NOTES			14. (Leave blank)		
16. ABSTRACT (200 words or less) <p>Research has continued at a low-level waste disposal facility to characterize the physicochemical species of radionuclides migrating in groundwater. This facility consists of an unlined basin and connecting trench which receives effluent water containing low levels of a wide variety of fission and activation products and trace amounts of transuranic radionuclides. The effluent water percolates through the soil and a small fraction of it emerges at seepage springs located some 260 meters from the trench. The disposal basin and trench are very efficient in retaining most of the radionuclides, but trace amounts of a number of radionuclides existing in mobile chemical forms migrate in the groundwater from the trench to the springs. This facility provides the opportunity for characterizing the rates and mechanisms of radionuclide migration in groundwaters, identifying retardation processes, and validating geochemical models.</p>					
17. KEY WORDS AND DOCUMENT ANALYSIS Radionuclide Migration Groundwater Low-level Waste			17a. DESCRIPTORS		
17b. IDENTIFIERS/OPEN-ENDED TERMS					
18. AVAILABILITY STATEMENT Unlimited			19. SECURITY CLASS (This report) Unclassified		21. NO. OF PAGES
			20. SECURITY CLASS (This page)		22. PRICE \$

1. TITLE AND SUBJECT Radioactive Wastes in Groundwater Annual Progress Report for 1982		2. AUTHOR(S) K. H. Axel and R. L. Stodnick D. E. Robertson, A. R. Jorde		3. REPORTING ORGANIZATION NAME AND MAILING ADDRESS Pacific Northwest Laboratory P.O. Box 999 Richland, WA 99352		4. PERFORMING ORGANIZATION NAME AND MAILING ADDRESS U.S. Nuclear Regulatory Commission Office of Health, Safety, and Waste Management Division of Health, Safety, and Waste Management Washington, D.C. 20555		5. DATE REPORT COMPLETED NOVEMBER 1982		6. DATE REPORT ISSUED NOVEMBER 1982		7. REPORT NUMBER PNL-2773		8. REPORT NUMBER (NRC) NRC-3554			
9. PROJECT TASK WORK UNIT NO. 8-2300		10. PROJECT TASK WORK UNIT NO. 8-2300		11. DATE 1982		12. DATE 1982		13. DATE 1982		14. DATE 1982		15. DATE 1982		16. DATE 1982			
17. SUMMARY Research has continued at a low-level waste disposal facility to characterize the physicochemical species of radionuclides migrating in groundwater. This facility consists of an unlined basin and connected trench which receives effluent water containing low levels of a wide variety of fission and activation products and trace amounts of transuranic radionuclides. The effluent water percolates through the soil and a small fraction of it emerges at seepage springs located some 300 meters from the trench. The physical basin and trench are very old and contain most of the radionuclides, but trace amounts of a number of radionuclides are detected in seepage water. This facility provides the opportunity for characterizing the rates and mechanisms of radionuclide migration in groundwaters, identifying retardation processes, and validating analytical models.		18. ABSTRACT (200 WORDS MAX) Research has continued at a low-level waste disposal facility to characterize the physicochemical species of radionuclides migrating in groundwater. This facility consists of an unlined basin and connected trench which receives effluent water containing low levels of a wide variety of fission and activation products and trace amounts of transuranic radionuclides. The effluent water percolates through the soil and a small fraction of it emerges at seepage springs located some 300 meters from the trench. The physical basin and trench are very old and contain most of the radionuclides, but trace amounts of a number of radionuclides are detected in seepage water. This facility provides the opportunity for characterizing the rates and mechanisms of radionuclide migration in groundwaters, identifying retardation processes, and validating analytical models.		19. KEY WORDS AND DOCUMENT ANALYSIS Radioactive Wastes Groundwater Low-level waste		20. DISTRIBUTION STATEMENT Unlimited		21. SECURITY CLASSIFICATION UNCLASSIFIED		22. SECURITY CLASSIFICATION UNCLASSIFIED		23. SECURITY CLASSIFICATION UNCLASSIFIED		24. SECURITY CLASSIFICATION UNCLASSIFIED		25. SECURITY CLASSIFICATION UNCLASSIFIED	