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Radionuclide Distributions and Migration Mechanisms at Shallow Land Burial Sites

1982 Annual Report of Research Investigations on the Distribution, Migration and Containment of Radionuclides at Maxey Flats, Kentucky

Prepared by L. J. Kirby, Editor

Pacific Northwest Laboratory
Operated by
Battelle Memorial Institute

Prepared for
U.S. Nuclear Regulatory
Commission

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Prepared by
L. J. Kirby, Editor

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ABSTRACT

Subsurface waters at Maxey Flats are anoxic, have a high alkalinity and contain high concentrations of ferrous, sulfide and ammonium ions and organic carbon. The trench leachates are extremely variable in composition. Prominent radionuclides include ^3H , ^{60}Co , ^{90}Sr , ^{137}Cs , ^{238}Pu , ^{239}Pu , ^{240}Pu and ^{241}Am . A wide spectrum of dissolved organic compounds is present in the leachates, including EDTA, polar organics and decomposition products from the waste forms. Cobalt-60 and plutonium are present as EDTA complexes and ^{90}Sr and ^{137}Cs are associated with carboxylic acid type compounds. The chemistry of these waters changes drastically as they become oxic and plutonium becomes less mobile under these new conditions. Water enters the trenches by infiltration through the trench caps, through subsidence areas, and through interfaces between new landfill and the original soil. Lateral flow is very complex and slow, and apparently occurs mainly by fracture flow. The plastic infiltration barrier installed in 1981-1982 has been effective in reducing soil moisture if cracks and leaks are eliminated. To date, no direct evidence of radionuclide transport to offsite locations by subsurface flow has been confirmed. The offsite distribution of radionuclides, except for tritium, is comparable to the ambient fallout from nuclear weapons testing. Tritium concentrations in water offsite are orders of magnitude below MPC levels.

PREFACE

The research covered by this report was performed by Pacific Northwest Laboratory, Brookhaven National Laboratory, Los Alamos National Laboratory, and the University of California-Berkeley for the U.S. Nuclear Regulatory Commission (NRC). Research papers contained in this document are based on technical presentations made at the research review meeting in Slade, Kentucky, in October, 1982. Project monitors for NRC Maxey Flats research are Dr. Edward O'Donnell and Dr. George Birchard of the Waste Management Branch, Office of Nuclear Regulatory Research. Chief of the Waste Management Branch is Enrico F. Conti.

The report was compiled and edited by Dr. Lynn J. Kirby of Pacific Northwest Laboratory and includes research papers prepared by each of the participating laboratories listed above. The editor is indebted to W. H. Rickard and A. P. Toste of Pacific Northwest Laboratory; R. Dayal, R. F. Pietrzak, J. Clinton and M. Kinsley of Brookhaven National Laboratory; W. L. Polzer, E. H. Essington and E. B. Fowler of Los Alamos National Laboratory; and R. K. Schulz of the University of California-Berkeley for preparing the technical papers contained herein. Thanks are also extended to the many reviewers who read the first draft of this report and offered valuable suggestions and criticisms.

Previous reports in this series include NUREG/CR-1832, "Research at Maxey Flats and Consideration of Other Shallow Land Burial Sites," (March, 1981) and NUREG/CR-2383, "Radionuclide Distributions and Migration Mechanisms at Shallow Land Burial Sites: Annual Report of Research Investigators on the Distribution, Migration and Containment of Radionuclides at Maxey Flats, Kentucky," (July, 1982).

EXECUTIVE SUMMARY

BACKGROUND

The Maxey Flats, Kentucky, low-level waste (LLW) burial site is one of several commercial shallow land burial sites that were established in the eastern U.S. where rainfall is comparatively high. Greater problems are experienced with trench cap subsidence and infiltration of surface water in these areas than in the arid western sites. At Maxey Flats the interpretation of radionuclide movement is complicated by the fact that radioactivity could have spread by processes other than groundwater transport. For example, some of the trenches have accumulated excess amounts of water which has infiltrated through the trench caps and seepage has occurred from these trenches, releasing small amounts of the buried waste radionuclides. In addition, site repair work has resulted in some general low-level contamination of the area. Other known sources of contamination include atmospheric transport from the plume of an evaporator that was used to remove water from the trenches and the spillage of radioactive liquids during the active operation of Maxey Flats as a burial ground. Consequently, it is very difficult to differentiate between environmental contamination from these sources and radionuclide migration by groundwater transport. Although some radionuclide migration has been detected near burial trenches at Maxey Flats, no offsite subsurface movement of radionuclides other than tritium has been found.

A concise history and description of the Maxey Flats site from its opening in 1963 to cessation of disposal operations in 1977 is summarized by Clancy and others (1981). In October, 1974, the Commonwealth of Kentucky informed the U.S. Atomic Energy Commission, the predecessor of the Nuclear Regulatory Commission (NRC), of the results of their special six-month environmental study at Maxey Flats. The study, published in December, 1974, concluded that the disposal site was contributing radioactivity to the local environment, but at levels which did not present a public health hazard. The study identified ^3H , ^{60}Co , ^{89}Sr , ^{90}Sr , ^{134}Cs , ^{137}Cs , ^{238}Pu , and ^{239}Pu in individual samples in the unrestricted environment. The radionuclide concentrations considered significant for purposes of this study ranged from slightly to several orders of magnitude (for certain individual samples) above concentrations that were defined as ambient. The Commonwealth of Kentucky then recommended further studies at the site to assess the long-range health and safety significance of their findings. Since that time, numerous studies have been carried out by the Commonwealth, their contractors, the U. S. Geological Survey (USGS), and contractors for the NRC and the Department of Energy (see Clancy and others, 1981; Kirby and others, 1981 and 1982; and Zehner, 1979).

To determine the nature and extent of any radionuclide migration from waste burial trenches, the processes which are occurring relative to degradation of radioactive materials within the burial trenches must be known. The chemical and physical characteristics of the trench leachates, the key geochemical controls governing the leachate characteristics, the chemical forms of the leached radionuclides, the mobility of these radionuclides, the subsurface and surface radionuclide transport processes, the biological uptake, the development of environmental monitoring strategies and other factors which influence the long-term fate of the waste radionuclides must be determined. A research program utilizing the background provided by prior Brookhaven National

Laboratory (BNL) trench chemistry studies and USGS groundwater studies and encompassing the factors above was initiated in 1979 with Pacific Northwest Laboratory (PNL) as coordinator for the research performed at Maxey Flats by PNL, BNL, Dames & Moore, Los Alamos National Laboratory (LANL), the University of Arizona, the University of California-Berkeley (UCB), the University of California-Los Angeles.

OBJECTIVES

PNL has assisted in coordinating the NRC research program at Maxey Flats since 1979 to establish and carry out a unified and comprehensive study of the problems specific to that site and to obtain generic information that may be useful in setting criteria for decommissioning of existing sites and for licensing of future commercial LLW burial sites. The objectives of this broad, multidisciplinary, multilaboratory program include determining:

- Radiochemical and chemical composition of leachates in waste burial trenches;
- Subsurface migration rates of radionuclides and the chemical, physical, biological, and hydrogeological factors which affect this migration;
- Areal distribution of radionuclides at commercial shallow land burial sites and the factors responsible for this distribution;
- Concentrations of radionuclides in vegetation both on and off site and the uptake of radionuclides by representative agricultural crops;
- Atmospheric pathways for radionuclide transport and the mechanisms involved; and
- Engineering practices which influence the seepage of surface waters into the burial trenches.

The Commonwealth of Kentucky is concentrating their efforts on the stabilization and closure of the Maxey Flats Disposal Facility, and their primary objective in the present and future management of the facility must be to insure the protection of the general population living near the site from releases of radioactive materials. This will require a reasonable isolation of the radioactive wastes contained on site, such that any radioactive materials released to the environs do not result in an annual dose to man that exceeds recommended regulatory limits throughout the institutional and passive control phases of the site. In addition, the ALARA concept of maintaining radionuclide releases to the environs as low as reasonably achievable should continue to be an integral part of the management plan. The research at Maxey Flats is emphasizing those studies that will complete the information base required by the Commonwealth for developing decommissioning plans that will meet the objectives above.

The integrated research projects at Maxey Flats also respond to generic information needs for source term definition, chemical species determinations, mechanisms of groundwater flow, radionuclide transport mechanisms and monitoring methodology to assure waste containment and site stability. Specific research areas include (1) leachate source terms (BNL, PNL); (2) complexing and chelation processes (PNL, BNL); (3) chemical changes during radionuclide

transport (LANL, PNL); (4) types and mobilities of radionuclide species (PNL, BNL); (5) retardation mechanisms, soil moisture changes and mechanisms of groundwater movement in the unsaturated zone (LANL, UCB); (6) distribution coefficients for various soil/groundwater systems and laboratory validation of field-derived coefficients (BNL, LANL); (7) quantification of moisture movement through trench caps (UCB, LANL); methodology for field measurement of radionuclide movement (PNL, LANL); (8) state-of-the-art radioactivity survey systems, characterization of radionuclide distributions and determination of areas of contamination (PNL); and (9) ecological monitoring methodology (PNL).

EXPERIMENTAL FACILITIES

Three experimental areas have been established on the Maxey Flats shallow land burial site (see Section I, Figure 1). One has an experimental trench that was especially constructed for this program. It was instrumented and allows the study of actual groundwater transport of radionuclides on the site and of the behavior of new trenches which employ a variety of capping materials. The second experimental area is near an older waste-filled trench. These installations permit sampling for comprehensive evaluation of the factors involved in the stated research objectives and are located to permit the evaluation of trench caps. A third experimental area includes the lysimeter installations for the UCB research studies on water balance. The experimental areas provide a physical bond between the research projects of the various participating laboratories and enable a close integration of research results to satisfy overall program objectives.

The experimental installations were initiated in late 1979 with the construction of the experimental trench near waste trench 27 and the installation of porous cups and soil moisture cells near waste trench 19S. Details of these installations were reported in NUREG/CR-1832 and are reviewed in Section I of this report. These facilities have been used to provide samples for radionuclide and groundwater studies of regions of saturated and unsaturated flow and soil moisture data. The data obtained are providing information on radionuclide migration, chemical species, subsurface flow by saturated and unsaturated flow, trench cap design and surface drainage to control erosion.

A second series of sampling stations was installed late in 1980. Inert atmosphere wells were installed near the experimental trench to help maintain the initial oxidation state of the dissolved radionuclides in groundwater samples (Section I, Figure 2). At the same time, additional porous cups and soil moisture cells were installed near the experimental trench, and a large number of additional porous cups and soil moisture cells were installed in the study area near waste trench 19S (Section I, Figure 1). The installations accomplished in late 1980 have assisted in the development of a comprehensive picture of the hydrology of the zone between the waste trenches. Details of these installations are reviewed in Sections I, III and IV of this report.

These experimental facilities have permitted extensive sampling and other measurements to be made in conducting the research at Maxey Flats. The research is providing a basis for guidelines on the operation of existing commercial LLW shallow land burial (SLB) sites and on remedial action and decommissioning. In addition, it is helping us to identify long-term surveillance and maintenance requirements and site selection criteria for future sites.

RESEARCH REVIEW MEETINGS

Since the research program was started at Maxey Flats, several formal research review meetings have been held to discuss the research findings and plan additional research. The first research review meeting was held at NRC headquarters in July, 1980, and technical papers from this meeting are published in NUREG/CR-1832. The second research review meeting was held in Frankfort, Kentucky, in July, 1981, and technical papers from this meeting are published in NUREG/CR-2383.

The third research review meeting to review the research program and policy on NRC research at the Maxey Flats LLW disposal site was held October 26-28, 1982, at the Natural Bridge State Park, Kentucky and at the Maxey Flats site and the technical presentations made at that meeting form the basis for this report. Participants included representatives of NRC's Offices of Nuclear Regulatory Research (RES), Nuclear Material Safety and Safeguards (NMSS) and State Programs (OSP). Other participants included representatives of PNL, BNL, LANL, UCB, USGS, the Commonwealth of Kentucky, Hittman Nuclear and Development Co., Illinois Geological Survey, Morehead State University and Oak Ridge National Laboratory. A tour of the Maxey Flats LLW disposal site was conducted to review the physical features of the site, to view current on-site operations and to examine the on-site experimental installations of the various contractors. Following a summary review of the current state of knowledge concerning the site, the NRC contractors' research projects were reviewed, and discussions held of problem areas and further research needs for bringing about a closure of the site.

The Commonwealth of Kentucky is anxious to permanently close the Maxey Flats site. Their major concerns include trench cap rehabilitation and water management, tritium immobilization and the handling and storage of evaporator residues. To assist them in their deliberations, an additional meeting for discussions of research observations at Maxey Flats that are relevant to site closure was held November 30 and December 1, 1982, at USGS offices in Reston, Virginia. Participants included representatives from NRC (RES, NMSS and OSP) and representatives of PNL, BNL, LANL, UCB, USGS and the Commonwealth of Kentucky. The panel identified at least 14 specific issues which should be considered in developing a closure plan for the Maxey Flats facility, all of which generally stem from certain site conditions: 1) subsidence of waste trench covers, 2) water accumulation in the trenches, 3) high tritium concentrations and complexed forms of other radionuclides in waste trench leachates and 4) complicated hydrogeology which makes prediction of subsurface radionuclide transport and radiological surveillance difficult. An informal report was distributed by NRC (RES) following the meeting.

RESEARCH OBSERVATIONS

Several lessons have been learned from the research at Maxey Flats:

- Adequate trench cap design and trench cap integrity are essential to prevent water from entering the waste trenches;
- Some degree of soil permeability may be needed at waste disposal sites. Sites in materials of low permeability or trenches lined

with infiltration barriers may result in water-filled disposal trenches unless provision is made to remove infiltrating water.

- Many features of Maxey Flats are probably similar to those that will be experienced at new sites; these include similar chemical species, wet waste, anoxic conditions, leaching of waste forms, complex leachates.

The research program at Maxey Flats has provided essential information on subsurface water chemistry, chemical species of radionuclides, modes of water entry into the waste trenches, mechanisms of subsurface flow, water balance, surface distributions of radionuclides and ecological monitoring methodology. The present status of these research studies is summarized in the following paragraphs.

Subsurface Water Chemistry

The trench leachates at Maxey Flats are highly anoxic, have a high alkalinity, and high concentrations of ferrous, sulfide and ammonium ions and organic carbon. The most prominent radionuclides derived from the waste forms include ^3H , ^{60}Co , ^{90}Sr , ^{137}Cs , 238 , 239 , ^{240}Pu and ^{241}Am . The trench leachates are highly variable from one trench to another and also within sections of a given trench. A wide spectrum of dissolved organic compounds is present in the leachates, including both hydrophilic and hydrophobic compounds. These compounds include complexing agents, polar organic compounds, naturally occurring compounds and organic compounds present in the waste or derived from decomposition of the waste. Ethylenediaminetetraacetic acid (EDTA) is the major organic component and evidence points to the presence of ^{60}Co and 235 , 239 , ^{240}Pu complexes with EDTA. Strontium-90 and ^{137}Cs appear to complex with carboxylic acid type compounds. The chemistry of these waters changes drastically if conditions are changed by movement from anoxic to oxic environments. Significant chemical changes include decreasing the pH, increasing the Eh and decreasing the organic carbon content. The interactions between iron, EDTA and Pu^{+3} during migration from the trenches result in the enhancement of Pu^{+3} adsorption by the soil during migration and plutonium is made less mobile by these chemical changes.

Water Entry into the Trenches and Subsurface Flow

Prior to installing a plastic infiltration barrier over the trenches at Maxey Flats in 1981-82, water levels had risen in the trenches, necessitating pumping the excess water to an on-site evaporator for removal. Water accumulated in the trenches by infiltration through the trench caps and subsidence areas, and to a lesser extent through interfaces between new landfill and the original soil. Lateral flow is very complex and slow, and apparently occurs mainly by fracture flow. The plastic infiltration barrier has been effective in reducing soil moisture content if there are no leaks in the cover. Lysimeter experiments have been initiated to enable prediction of site functions as affected by various types of site management and allow complete water balance studies at the Maxey Flats site. Measurements of radionuclides, organic compounds and inert groundwater tracers have demonstrated that communication exists on site between waste trench 27 and the experimental trench and inert atmosphere wells. The groundwater flow patterns in this region are very complex and have been influenced in the past by pumping water to the evaporator and by water

infiltration. Since the installation of the flexible vinyl infiltration barrier over the waste trenches and cessation of pumping activities, flow patterns have stabilized and the preferred direction of subsurface flow on site is from waste trench 27 toward the experimental trench and inert atmosphere wells. To date, no direct evidence of radionuclide transport at Maxey Flats to offsite locations by subsurface flow has been confirmed.

Surface Distribution of Radionuclides

Surface contamination by radionuclides has been retained mainly within the restricted area at Maxey Flats. Surface sediments in areas adjacent to the site, primarily on the west side, contain ^{60}Co in concentrations greater than fallout. The origin of the ^{60}Co is from surface runoff into the adjacent woods. Slightly elevated concentrations of ^{238}Pu have also been observed in a few offsite soils in drainage areas and are presumably derived from slightly contaminated surface runoff. Measurements made to date indicated that offsite contamination by radionuclides has not resulted from subsurface transport, except possibly for tritium. Elevated concentrations of tritium have been observed in soil and vegetation surrounding the site. The main source is presumably from the evaporator, except on the western perimeter (near Trench 31) where some vegetative uptake from subsurface flow may be occurring.

The on-site surface distribution of ^{60}Co and ^{137}Cs is very patchy and low in concentrations. Independent distribution patterns were observed for ^{60}Co , ^{90}Sr , ^{137}Cs , ^{238}Pu , ^{239}Pu , ^{240}Pu and ^{241}Am . The offsite distribution of radionuclides, except for tritium, is comparable to the ambient fallout from nuclear weapons testing. Tritium concentrations are orders of magnitude below MPC levels.

Ecological Monitoring

Ecological field sampling performed at Maxey Flats has evaluated a broad spectrum of radionuclides in leaves, forest floor litter and surface soil, but only ^3H and ^{60}Co appear to be derived from the disposal site. Even these radionuclides are at only slightly elevated levels - well below the MPC's for drinking water. These surveys indicate that leaf fall is a cost-effective, nondestructive sampling procedure that can be incorporated into ecological monitoring programs to indicate migration or lack of migration for shallow land burial sites. Tree sap and water from transpiring leaves have been collected and analyzed for tritium, indicating that tritium uptake by deeprooted trees has potential to serve as a biomonitor of subsurface movement of water from burial sites. Trees offer an effective long-term monitoring device for tritium and possibly other mobile radionuclides and could serve as an early warning system for migration of radionuclides from waste disposal sites. A tree could be used for at least 100 years for monitoring purposes. Trees and other vegetation permit sampling that isn't possible with monitoring wells that do not intercept a fracture and may be dry. The trees and vegetation seek out water and provide the opportunity to sample larger and otherwise inaccessible regions of soil.

RELEVANCE OF LLW RESEARCH

Much of the research program at Maxey Flats has been geared to meet the needs of the Commonwealth of Kentucky as they finalize their plans for site stabilization and closure. In fact, most LLW research to date has been directed toward understanding and resolving problems at existing LLW SLB sites. This research has indicated that there is a need for systematic measurement and surveillance of LLW disposal to provide an early warning of poor or unacceptable performance of a LLW facility in terms of radionuclide migration off-site. There is a long-term need to identify means for evaluating effective site confinement and long-term site performance. Technology to effect site stability in humid environments may need further development, including engineering methods appropriate to soil/climate combinations of the eastern United States. Soils play a complex role in affecting migration of waste radionuclides, as do subsurface water chemistry, chemical forms of radionuclides, modes of water entry into waste trenches, mechanisms of subsurface water flow and water balance within the burial system. Additional study of the radionuclide migration mechanisms in a broad range of soils is desirable.

The SLB sites that will be chosen under the newly formed state compacts will likely conform to the siting criteria contained in 10 CFR 61. It is likely that these sites will encompass a more extensive range of characteristics and transport phenomena than has been studied to date, and LLW research will be focused on a broader range of site performance variables than those investigated at Maxey Flats, including the impact on effecting site closure.

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SECTION I

CHEMICAL SPECIES OF RADIONUCLIDES AT THE
MAXEY FLATS, KENTUCKY SHALLOW LAND BURIAL SITE

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SUMMARY

The primary purpose of this project is to develop an understanding of chemical processes that significantly influence the migration of radionuclides at commercial low-level waste burial sites. Chemical measurements of waste trench leachate and identification of chemical changes in leachate during migration will provide a basis for geochemical waste transport models. This project will produce for the U.S. Nuclear Regulatory Commission (NRC) information to support guidance for implementation of 10 CFR 61, particularly in the development of criteria for commercial low-level waste disposal site selection, management, permanent closure and monitoring. This project will also produce information needed by the Commonwealth of Kentucky as they finalize plans to stabilize, close and monitor the Maxey Flats site.

CHEMICAL FORMS: INORGANIC AND ORGANIC RADIONUCLIDE SPECIES

To minimize solution degradation and duplicate actual field conditions as closely as possible, on-site chemical separations employing tracers and organic ligand separations have been performed. Following field trips to perform in situ chemical separations of waste trench leachate and inert atmosphere well water samples of Maxey Flats, we have performed detailed radionuclide and organic analyses. Analysis of the field-separated solutions from chromatographically fractionated water samples has revealed a complex pattern of association between radionuclides and organic compounds in these waters.

Ethylenediaminetetraacetic acid (EDTA) is the major organic compound in water from waste trenches 27 and 19S and in water from inert atmosphere well W2NA. EDTA-like species of molecular weights 219, 244 and 288 have been measured in water from waste trenches 27 and 19S and EDTA-like species of molecular weights 219 and 244 were measured in water from well W2NA. EDTA and EDTA-like species were not detected in inert atmosphere wells W1N, W3N and W3NA or in experimental trench sumps S4 and S5. The similarity with EDTA between the mass spectra of the EDTA-like species, and therefore their proposed structures, suggests that they arise from the degradation of EDTA.

EDTA and EDTA-like species coelute with alpha-emitting radionuclides and ^{60}Co . Evidence points to the migration of plutonium as an EDTA complex. Polar organic compounds (e.g. palmitic and stearic acids) may influence the migration of ^{90}Sr and ^{137}Cs . The absence of EDTA in inert atmosphere wells W1N, W3N and W3NA or in sections 4 and 5 of the experimental trench, combined with radionuclide concentration data, provides evidence to support the observed specific communication between waste trench 27 and inert atmosphere well W2NA.

Analysis of hydrophobic organic compounds in waste trench and inert atmosphere well water samples has shown that most of these compounds are present at parts-per-billion levels. Measurement of a nonradioactive tracer (pentafluorobenzoic acid) added during construction of the experimental trench at Maxey Flats has demonstrated that infiltration of water from the experimental trench area into waste trench 27 has occurred. The presence of two barbiturates in waste trench 27 and also in inert atmosphere well W2NA supports the finding of a very specific communication between these two sampling points.

Papers and presentations during the past year based on this research include:

- L. J. Kirby, A. P. Toste, W. H. Rickard and D. E. Robertson, "Radionuclide Characterization, Migration and Monitoring at a Commercial Low-Level Waste Disposal Site," IAEA-CN-43/470, PNL-SA-10882 presented at the International Conference on Radioactive Waste Management, International Atomic Energy Agency, Seattle, Washington, May 16-20, 1983.
- A. P. Toste, L. J. Kirby and T. R. Pahl, "Role of Organics in the Subsurface Migration of Radionuclides in Groundwater," PNL-SA-10882 presented at the Symposium on Geochemical Behavior of Disposed Radioactive Waste at the 185th National Meeting, American Chemical Society, Seattle, Washington, March 20-25, 1983.
- A. P. Toste, L. J. Kirby, D. E. Robertson, K. H. Abel, R. W. Perkins, "Characterization of Radionuclide Behavior in Low-Level Waste Sites," PNL-SA-10814, presented at the 1982 Nuclear Science Symposium, Institute of Electrical and Electronic Engineers, Washington, D.C., October 20-22, 1982.
- L. J. Kirby and A. P. Toste, "Chemical Characteristics, Migration and Fate of Radionuclides at Commercial Shallow Land Burial Sites," PNL-SA-10697, presented at the Fourth Annual Participants' Information Meeting, U. S. Department of Energy Low-Level Waste Management Program, Denver, Colorado, August 31-September 2, 1982; ORNL/NFW-82/18, pp. 477-503, 1982.

SUBSURFACE MIGRATION AND INFILTRATION STUDIES

During the past year, we have continued sampling the porous cups, experimental trench sumps and inert atmosphere wells on a regular monthly basis, weather permitting. We have also sampled three of the E-series wells around the Maxey Flats site. Analyses of the experimental trench and inert atmosphere well water samples for radionuclides and organic compounds verify that subsurface migration of radionuclides has occurred over limited distances within the Maxey Flats restricted area. With the possible exception of tritium, subsurface migration to points outside the restricted area has not been a significant source of contamination by radionuclides of the environs adjacent to the Maxey Flats site.

Following the installation of the inert atmosphere wells at Maxey Flats, radionuclide concentrations in water samples were relatively constant over the

two-year period ending in December, 1982. Immediately after the shutdown of the evaporator and cessation of pumping at the end of 1982, tritium concentrations increased dramatically in the wells farthest south from waste trench 27, indicating that major changes in groundwater flow were occurring. This occurred primarily because the trench leachates were no longer being pumped to the evaporator and infiltration of surface runoff water was prevented by the installation of the flexible vinyl infiltration barrier over the burial area. Following this initial rapid change over a two-month period, water levels and radionuclide concentrations have once again begun to exhibit little change, indicating that the groundwater table has stabilized.

SPECIFIC RADIONUCLIDE MAPPING AT COMMERCIAL SHALLOW LAND BURIAL SITES

Field sampling to determine radionuclide distributions in the forest surrounding the Maxey Flats restricted area has shown that tritium levels adjacent to the site have been influenced by site activities, such as operation of the evaporator. It is also possible that tritium levels, especially in off-site springs and seeps, may be influenced by subsurface flow. If this latter supposition proves true, then it is important to know whether elevated tritium levels in these springs and seeps are an early warning that other radionuclide levels might also be slightly elevated. To answer this question and complete the specific radionuclide mapping, we have performed additional in situ gamma-ray spectrometric analyses at selected springs and seeps around the site. Preliminary analysis of the data indicates that no waste-derived radionuclides, other than tritium, are present in these springs and seeps and that these sampling locations are not in direct communication with the waste-filled area.

Analysis of the soil and vegetation samples collected during field trips to the Maxey Flats site was conducted during the reporting period, and assembly of the analytical data for preparation of a topical report on specific radionuclide distributions at the Maxey Flats site is continuing. This report will include a summary of the radionuclide content of vegetation from the restricted area and adjacent areas and should help to indicate the relative importance of soil uptake versus uptake via foliar adsorption. In this report, we will emphasize those radionuclides which are of greatest concern from an environmental and health standpoint.

ECOLOGICAL MONITORING AT COMMERCIAL SHALLOW LAND BURIAL SITES

Ecological field sampling performed at Maxey Flats has evaluated a broad spectrum of radionuclides in leaves, forest floor litter and surface soil but only ^3H and ^{60}Co appear to be derived from the disposal site. Even these radionuclides are at only slightly elevated levels - well below the MPC's for drinking water. These surveys indicate that leaf fall can be a cost-effective, efficient way to estimate the annual contribution of radionuclides to the forest floor of oak-hickory forests. Tree sap and water from transpiring leaves have been collected and analyzed for tritium, indicating that tritium uptake by deeprooted trees has potential to serve as a biomonitor of subsurface movement of water from burial sites. These surveys have indicated that biomonitors may be useful as indicators of radionuclide migration from shallow land burial sites.

Tritium measurements in systemic water from trees adjacent to the Maxey Flats site were completed for samples collected during July, 1982 and October, 1982. Tritium concentrations for leaf samples from comparable locations for the two sampling periods do not show evidence of seasonal variation at these locations. Data from these samples provide a basis on which to evaluate the effectiveness of the infiltration barrier installed over most of the burial site. They also provide a basis for evaluating the effect of the evaporator on radionuclide levels in the environs adjacent to the Maxey Flats restricted area. Tritium concentrations from trees sampled in July, 1982 showed about a ten-fold decrease over similar measurements conducted in 1981. The data indicate that the infiltration barrier installed over most of the site in the fall of 1981 has been effective in reducing infiltration into the trenches.

TECHNICAL PROGRAM COORDINATION

Pacific Northwest Laboratory (PNL) assisted NRC in the preparation of the agenda for discussions of research observations at Maxey Flats which are relevant to site closure. This meeting was held November 30 and December 1, 1982 at USGS offices in Reston, Virginia. Research panel members included representatives of NRC's offices of Nuclear Regulatory Research, Nuclear Material Safety and Safeguards, and State Programs. Other panel members included representatives of PNL, Los Alamos National Laboratory (LANL), the University of California-Berkeley (UCB), Brookhaven National Laboratory (BNL), the U.S. Geological Survey (USGS) and the Commonwealth of Kentucky. PNL also assisted NRC in the drafting and revision of a report on the deliberations of this panel, entitled "Initial Review of Research Observations at Maxey Flats which are Relevant to Site Closure," which has been distributed to the participating Offices, Agencies and Laboratories.

PNL assisted in the preparation of the agenda for an annual review of policy and research progress of NRC research at the Maxey Flats low level waste disposal site. This meeting was held October 26-28, 1982 at the Natural Bridge State Park, Slade, Kentucky, and at the Maxey Flats site. Participants included representatives of NRC's offices of Nuclear Regulatory Research, Nuclear Material Safety and Safeguards and State Programs. Other participants included representatives of PNL, LANL, UCB, BNL, USGS, the Commonwealth of Kentucky, Hittman Nuclear and Development Co., Illinois Geological Survey, Morehead State University and Oak Ridge National Laboratory. An informal report was jointly prepared by PNL and NRC and distributed to the participating Offices, Agencies and Laboratories.

INTRODUCTION

Commercial shallow land burial sites located in the eastern half of the country where rainfall rates are relatively high experience greater problems with subsidence and seepage of water into and from the burial trenches than those located in the more arid regions. Interpretation is complicated by the fact that there are several processes for radionuclide transport besides subsurface transport. For example, at both Maxey Flats and West Valley, the burial trench cap material subsided and the reworking of the areas to form new caps has resulted in localized spread of contamination. At Maxey Flats additional known sources of contamination include atmospheric transport from the evaporator plume and spillage of radioactive liquids. Consequently, it is very difficult to differentiate between environmental contamination from these sources and radionuclide migration by subsurface aquifer transport.

One of the most important factors to be considered during the long-term isolation of radioactive wastes at commercial LLW burial sites is the subsurface migration of radionuclides, which depends, among other things, on the chemical forms of the radionuclides. The oxidation state, ionic form, and the formation of complexes or chelates with organic ligands can markedly influence radionuclide migration. Therefore, determination of the precise chemical species of radionuclides that have migrated is essential for an accurate evaluation of the long-term performance of commercial shallow land burial sites. It is also essential to identify the organic and inorganic compounds and ionic species which are present in buried waste or can be generated in situ by chemical reactions and subsequently participate in the formation of the chemical species that may be shown to migrate.

OBJECTIVES

The primary purpose of this PNL project is to develop an understanding of the chemical processes that influence radionuclide migration at commercial LLW burial sites. Chemical measurements of waste trench leachate and identification of chemical changes in chemical forms that occur during migration are being made and will provide a basis for geochemical waste transport models. This project will produce for NRC information to support guidance for implementation of 10 CFR 61, particularly in the development of criteria for commercial LLW disposal site selection, management, permanent closure and monitoring.

Specific objectives of this project with respect to measurements to be made at existing commercial sites are:

- Define the actual chemical species of the radionuclides which are migrating by subsurface routes;
- Identify the chemical characteristics of the trench leachate which retard or enhance radionuclide mobility;
- Determine the chemical changes in leachate properties which result from installation of infiltration barriers such as the flexible vinyl covers at Maxey Flats;

- Provide the chemical and radiochemical input parameters essential for hydrological/geochemical modeling of subsurface radionuclide transport;
- Determine the factors responsible for the areal distributions of surface radionuclides and develop improved procedures for monitoring;
- Develop and test post-closure monitoring protocols that can be used at Maxey Flats and test the applicability of these protocols to operational and post-operational monitoring at other commercial sites; and
- Assist in coordinating LLW research projects for NRC.

Field measurements at shallow land burial sites provide unique opportunities to identify in actual waste burial situations the chemical and geochemical parameters which retard or enhance radionuclide mobility at LLW burial sites. The work at Maxey Flats also responds to the NRC Office of State Programs' request for information on the areal distribution of radionuclides and the extent of subsurface transport of radionuclides at that site. This information is needed by the Commonwealth of Kentucky as they finalize plans to stabilize, close and monitor the Maxey Flats site.

SUMMARY OF PRIOR EFFORTS

Under this research program, PNL assists in coordinating NRC-sponsored LLW research, which has included PNL studies on chemical species and areal distributions of radionuclides, work on trench water chemistry by BNL, plant uptake studies by the University of California-Los Angeles, engineering studies by the University of Arizona, unsaturated flow studies by LANL and UCB, and water and mass balance studies by the Commonwealth of Kentucky.

To conduct experiments for determining the subsurface transport of radionuclides from existing waste burial trenches, the first two experimental areas were established at the Maxey Flats, Kentucky LLW disposal facility. This required the cooperation of several national and state agencies, together with the NRC contractors, for successful implementation. These experimental areas included:

- An experimental slit trench installed during the last quarter of FY 1979 and first quarter of FY 1980; and
- Fourteen inert atmosphere sampling wells installed in undisturbed soil adjacent to the experimental slit trench during the last quarter of FY 1980. A comprehensive array of porous cups and soil moisture cells was also installed for the LANL and UCB programs at this time.

The experimental areas have been described in NUREG/CR-1832, Section IV and NUREG/CR-2383, Section I and are illustrated in Figures 1 and 2 of this report. These experimental areas support research studies by PNL, LANL, UCB and BNL.

The two experimental areas are enabling samples to be taken for the study of chemical species of radionuclides, saturated and unsaturated flow, nonradioactive tracer movement, trench cap engineering and drainage, plant uptake, and total water balance by the laboratories participating in research at Maxey Flats. These experiments have provided needed information on rates and mechanisms of subsurface transport of radionuclides from waste burial trenches by both saturated and unsaturated flow and promise to provide more detailed information on subsurface flow at the site.

PNL research (NUREG/CR-1832, page IV-8) has demonstrated that plutonium in water from the experimental trench and in waste trench 27 leachate was present in highly complexed, anionic, reduced (trivalent and tetravalent) species, in basic agreement with observations by Cleveland and Rees (1981). EDTA is the major organic complexing component in waste trench 27 leachate, but other polar, water-soluble organic compounds are also present (NUREG/CR-2383, page I-17). Plutonium and EDTA co-elute during steric exclusion chromatography of Maxey Flats trench and well waters, and evidence points to the migration of plutonium as an EDTA complex. Polar organic compounds (e.g. palmitic and stearic acids) may influence the migration of ^{90}Sr and ^{137}Cs . These studies have demonstrated the need to determine the effect of the conditions existing in waste trench water at Maxey Flats on the stability of the plutonium-EDTA complex, the conditions under which complexes of plutonium, americium, cobalt and strontium can be decomposed and/or sorbed on the geologic media, and the need to separate and measure the concentrations of hydrophilic organic complexing agents that may affect the migration of radionuclides present in waste trench leachate.

Changes in tritium concentrations in water from the experimental trench and in inert tracers (e.g., sodium bromide) which were added to the trench (NUREG/CR-1832, pages IV-10 and IX-6), confirm that subsurface flow does occur rather rapidly. While increases in water level have occurred in the experimental trench, the absence of tracers in the water indicates that these increases have occurred without movement through the different trench caps installed on the five sections of the experimental trench (NUREG/CR-2383, page I-18).

Field measurements have been performed by PNL at the Beatty, Nevada (NUREG/CR-1524), and Maxey Flats, Kentucky (NUREG/CR-2383, Section II and NUREG/CR-1832, Section IV) burial sites to help determine the areal distribution of radionuclides at these sites and the factors responsible for this distribution. Field measurements were also performed adjacent to the Maxey Flats facility, and confirmed that contamination is largely contained within the restricted area at this burial site. The areal distribution of radionuclides at Maxey Flats has been influenced by site operation and maintenance activities, surface contamination and runoff, deposition from the evaporator plume, and the actions of burrowing animals or deep-rooted trees. Vegetational and surface contamination on site and near site are quite low; of the gamma-ray-emitting radionuclides measured, only ^{60}Co exceeds commonly observed fallout levels. The average concentrations in surface soil at Maxey Flats are comparable to concentrations resulting from normal fallout in other areas of high rainfall. Tritium concentrations in water near the site have been influenced by surface runoff and by condensation from the evaporator plume.

Ecological field sampling performed at Maxey Flats (NUREG/CR-1832, Section V, and NUREG/CR-2383, Section III) has evaluated a broad spectrum of radionuclides in leaves, forest floor litter and surface soil, but only ^3H and ^{60}Co appear to be derived from the disposal site. Even these radionuclides are at only slightly elevated levels and are comparable to ambient fallout levels. Collections of freshly fallen tree leaves indicate that leaf fall collection is a cost-effective, nondestructive sampling procedure that can be incorporated into ecological monitoring programs to indicate migration or lack of migration from LLW sites. Tree sap and water from transpiring leaves have been collected and analyzed for tritium, indicating that tritium uptake by deeprooted trees has potential to serve as a biomonitor of subsurface movement of water from burial sites. The surveys have indicated that biomonitors may be useful as indicators of radionuclide migration at LLW sites.

Remaining important areas of research include the fate of mobile (possibly complexed) radionuclide species after leaving the trench environment, the control of these species within the site boundaries, remedial action that can be taken to halt this mobility, and whether complexing agents such as EDTA can be effectively destroyed in an aerobic environment.

Important observations from research conducted by PNL at Maxey Flats include:

- Identification of the magnitude of transport over short distances within the burial site by subsurface flow;
- Characterization of some of the important chemical species including plutonium-EDTA complexes which are responsible for subsurface migration;
- Identification of surface runoff from the site as a principal source for off-site radionuclide accumulation in vegetation;
- Determination of the off-site distribution of radionuclides at Beatty, Nevada, and Maxey Flats, Kentucky; and
- Establishment of the complexity and variability of waste trench leachates as source terms for the migration studies. (PNL research complements the comprehensive analyses performed on waste trench leachate by BNL. See, for example, NUREG/CR-2383, Section IV, and NUREG/CR-1832, Section III.)

These research observations and related observations from the research performed at Maxey Flats by BNL, LANL, UCB, the University of Arizona and the University of California-Los Angeles are described in NUREG/CR-2383 and NUREG/CR-1832.

EXPERIMENTAL METHODS

EXPERIMENTAL SLIT TRENCH AND INERT ATMOSPHERE WELLS

An experimental slit trench was constructed adjacent to an existing waste-filled trench at Maxey Flats in 1979. The experimental trench was designed to accommodate a variety of experiments by the laboratories participating in research at Maxey Flats. Sumps were installed to permit sampling for radionuclide and non-radioactive tracer studies of saturated flow. Porous cups and soil moisture cells were installed in the trench wall, cap and adjacent area for the study of unsaturated flow and moisture gradients near the experimental trench. Nonradioactive tracers were included to monitor groundwater movement to and from the experimental trench and to evaluate the permeability of the trench caps to water movement and to root penetration. Several small vegetation plots were established to evaluate potential cover crops, and engineering studies were included to evaluate different trench caps and drainage systems. Details of trench construction are described in NUREG/CR-1832, Section IV, and are summarized in Table 1.

In a second and related construction effort in 1980, inert atmosphere sampling wells were installed in undisturbed ground adjacent to the experimental trench to study subsurface water that would not be influenced by the trench construction materials. The well caps were sealed, permanent sampling and gas lines installed, and the wells purged with argon. During and between sampling activities, the wells are maintained under an argon atmosphere to permit chemical separations to be made on water samples from the wells without the adverse effects of traces of oxygen on the chemical equilibria. The well design permits the determination of chemical species of dissolved radionuclides with minimal disturbance of the chemical balance between soil and groundwater.

Fourteen inert atmosphere wells were installed as part of an effort which also included the installation of sampling stations for unsaturated flow and soil solution studies near the experimental trench and in an undisturbed region of the Maxey Flats site between two old waste trench caps. Figure 1 shows the locations of these experimental installations relative to the existing waste-filled trenches. The placement of the inert atmosphere wells relative to the experimental trench and to waste trench 27 is presented in greater detail in Figure 2. Details of sampling station placement for the study of unsaturated flow and moisture gradients by LANL and UCB are given in NUREG/CR-2383, Sections V and VI.

Water samples were withdrawn using peristaltic pumps. Since their installation, up to eight of the wells have been productive sampling stations, but some wells provide water only on an intermittent basis. Several of the wells, mostly on the western end of the experimental trench near sections 4 and 5, have remained dry since installation. After sampling, the water samples are shipped to PNL for analysis for ^3H , ^{60}Co , ^{90}Sr , ^{137}Cs , ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Am and organic ligands. Tritium analyses are performed by liquid scintillation spectrometry and ^{90}Sr is chemically separated and counted using a beta proportional counter. Gamma-emitting radionuclides are analyzed by gamma-ray spectrometry using a Ge(Li) detector. Plutonium and americium are determined using solid state detectors and alpha energy analysis. Nonradioactive species

are determined by neutron activation analysis using the PNL subcritical neutron multiplier (Wogman et al. 1977), and by chemical and instrumental analysis.

IN SITU GAMMA-RAY SPECTROMETRY

The in situ gamma-ray spectrometry system is similar to systems used in previous research by PNL (Nielsen et al. 1977; Brodzinski 1980). It consists of a Princeton Gamma-Tech* coaxial intrinsic germanium diode coupled to a Canberra Series 80* multichannel analyzer and a cassette data recorder. A portable 1.5 kW Honda* generator supplies the electrical power. The detector is suspended from a tripod stand and can be positioned from ground level to a height of 1 meter. All field measurements at the Maxey Flats site were made with the detector 1 meter above ground level. Signal and power cables 30 meters long connect the detector to the analyzer, which is transported in a vehicle. The liquid nitrogen reservoir for the detector system has sufficient capacity to permit at least 12 hours of continuous operation.

For the measurements in the drainages adjacent to the restricted area, a portable backpack gamma-ray spectrometer system was used. The system consists of a Princeton Gamma-Tech* coaxial intrinsic germanium diode coupled to a Davidson Model 4106A* multichannel analyzer. Data acquisition is completed by memory transfer to a magnetic tape with a portable cassette recorder. This electronic package, together with a 140 volt d.c. Globe* gel/cell battery pack, is mounted on a specially adapted backpack frame and the detector is suspended from a modified photographer's tripod.

Calibration of the counting systems was made by comparing the disintegration rates of the naturally-occurring radionuclides in the soil with the count rates for the same radionuclides at each in situ counting location. The calibration factors so derived depend on the assumption that all the radionuclides are uniformly dispersed throughout the soil. By plotting the ratios of the in situ count rates to soil disintegration rates versus gamma-ray energy, calibration factors were derived for ^{137}Cs and ^{60}Co . All data reduction was accomplished in the laboratory using a PDP 11/44 computer and software developed for these analyses. The radionuclides measured include the naturally-occurring radionuclides ^{40}K , ^{208}Tl , ^{212}Pb , ^{214}Pb , ^{212}Bi , ^{214}Bi , and ^{228}Ac , as well as ^{60}Co and ^{137}Cs and other exogenous radionuclides. Thorium-228 is determined from its daughter concentrations.

Soil samples were collected from each location where a count was made and returned to the laboratory for analysis. Samples were taken at the site surface at counting locations within the restricted area. Two soil samples were taken wherever possible at each counting location in the main drainage channels leading from the site, one at the surface and a second sample 15 cm below the surface. Analysis of the soil samples for up to twenty-four gamma-emitting radionuclides (e.g., ^{40}K , ^{208}Tl , ^{212}Pb , ^{212}Bi , ^{214}Bi , ^{228}Ac , ^{228}Th , ^{60}Co and ^{137}Cs) was performed with a Ge(Li) coincidence/anticoincidence counting system at PNL facilities in Richland, Washington. Destructive analysis was performed to determine the levels of ^{90}Sr , $^{238,239,240}\text{Pu}$ and ^{241}Am in selected soil samples

* The use of manufacturers' names and model numbers is for descriptive purposes and does not constitute an endorsement of any product.

using laboratory procedures similar to those developed for studies conducted for the Electric Power Research Institute (Robertson et al. 1981).

ORGANIC LIGAND ANALYSIS

Organic analyses for the initial survey study were performed on unfractionated water samples. Organic analyses for the speciation study were performed on fractionated water samples following steric exclusion chromatography (see Figure 3).

Fifty ml each of the unfractionated water samples were concentrated ten-fold by rotary evaporation prior to organic derivitization. The water samples set aside for chromatographic fractionation were also concentrated ten-fold and the pH adjusted to that of the original sample ($\sim$ pH 7.2 - pH 7.6). The solution was filtered, loaded on a Sephadex G-15 column, and chromatographed with redistilled water. Replicate runs were made, with and without blue dextran as a void volume marker. The column effluent was monitored by ultraviolet absorbance at 254 nm and collected using a fraction collector. Each column fraction was acidified with hydrochloric acid and divided into equal portions. One portion was used for destructive radionuclide analysis and the second portion was used for nondestructive analysis of gamma-emitting radionuclides and for analysis of organic compounds.

The aliquot of the Sephadex G-15 fraction remaining after gamma-ray analysis was extracted with chloroform to remove hydrophobic organic compounds and this extract set aside for analysis by gas chromatography (GC) and combined GC-mass spectrometry (GC-MS). The aqueous fraction containing hydrophilic organic compounds was evaporated to dryness under nitrogen. The residue of each fraction was then methylated with BF_3 /methanol at 100°C in a sealed vial. After cooling, chloroform was added, the mixture was transferred to a buffer solution (pH 7) and vortexed. Part of the chloroform layer, which contained the methylated hydrophilic organics, was then evaporated under nitrogen. The residue was redissolved in chloroform and an aliquot analyzed by GC and by GC-MS.

GC analyses were performed on a Hewlett-Packard 5880* gas chromatograph with an SE-52 column. 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. Tetramethyl-EDTA was used as an internal and external GC standard to quantify the various organic constituents in the GC samples.

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. The GC column was interfaced directly to the mass spectrometer. A mass range of

* The use of manufacturers' names and model numbers is for descriptive purposes and does not constitute an endorsement of any product.

50 to 400 amu was scanned every 1.0 sec by computer (HP-2100MX equipped with the HP-7920 Large Disc Drive).

ECOLOGICAL SAMPLING

For the first series of measurements, litter samples consisting of a mixture of dead leaves, small twigs, bark bits, nutshells and partially decomposed plant material were picked by hand from 0.32 m² circular plots at 18 locations on the forest floor near the east and west boundaries of the burial ground. A layer of surface soil about 2.5 cm thick was also collected from the area that was cleared of litter, exposing the underlying mineral soil. Additional collections were made near the same locations in early December to collect only the newly fallen autumn leaves.

In establishing formal sampling procedures, sixteen trees located along the western edge of the burial site were permanently marked with numbered metal tags. Three rectangular 0.5 m² wire baskets were placed beneath the canopy spread of each tree to serve as traps to collect samples of autumn leaf fall. The baskets were set out in early September and emptied in late November after the trees had dropped their leaves. In May, litter, surface soil and subsurface soil were collected from selected trees to relate the concentrations of radionuclides in newly fallen leaves with concentrations in the litter and soil beneath the tree canopies.

In mid-summer, leaves were collected from oak trees to obtain samples of leaf water for tritium analysis. To collect the leaf water, the leaves were sealed inside large translucent plastic bags and exposed to natural sunlight. Water vapor condensed on the inside bag walls. The droplets were drained into a corner of the bag and then dripped into vials and sealed for shipment to the laboratory. In the winter, sap from maple trees was collected by tapping the tree trunks in the fashion used in the commercial harvesting of sap to obtain maple sugar.

Samples of soil, leaves and litter were sealed in plastic bags for delivery to the laboratory, where they were placed into paper bags and oven-dried at 50°C. Dried samples of leaves and litter were milled to pass through a 1.0 mm screen. Each sample was thoroughly mixed and a 100-gram aliquot was used for gamma-ray spectrometric measurements. Tritium was determined by liquid scintillation spectrometry after the leaf water and tree sap samples were purified by distillation.

RESULTS AND DISCUSSION

CHEMICAL FORMS: INORGANIC AND ORGANIC RADIONUCLIDE SPECIES

The migration rates of radionuclides depend to a major degree on their chemical species. It is therefore extremely important that we determine chemical species in the waste burial trenches and in any water which has carried these radionuclides to our sampling points in the experimental trench and inert atmosphere sampling wells, or to springs some distances from the waste-filled

trenches. In this task we are determining as nearly as practicable the precise chemical forms for those radionuclides which are of greatest concern from an environmental and health standpoint. We expect to report the predominant oxidation states of plutonium, ^{241}Am , ^{60}Co , ^{137}Cs and ^{90}Sr and whether they are present as complexes, chelates, or as simple ions. The precise radiochemical and chemical parameters obtained from these studies will provide important basic information on the chemical species that develop under various burial conditions. These studies will serve as a basis for modeling of the Maxey Flats site and other commercial LLW sites.

Determination of the precise chemical species of radionuclides requires detailed information on the organic complexing compounds that are present in waste trench water and in other groundwater sources. The organic research required has therefore progressed in two major directions. First, we have surveyed the organic content in water samples from two waste trenches, from several inert atmosphere sampling wells and from two sections of the experimental trench. Second, we have identified radionuclide/organic associations that would help us to determine the exact chemical species of the complexed radionuclides, particularly plutonium.

Organic Compounds in Water Samples

We have analyzed water from two waste trenches (27 and 19S), from four inert atmosphere wells (W1N, W2NA, W3N and W3NA), and from two experimental trench sumps (S4 and S5). The GC-MS analyses of the fractionated water samples to determine the hydrophilic and hydrophobic organic compounds have been completed. The hydrophilic organic contents of these samples are summarized in Tables 2-5, inc. The hydrophobic organic compounds present in the same samples are summarized in Tables 6-9, inc.

The chelating agent EDTA is the major hydrophilic species in water from waste trenches 27 and 19S and in water from inert atmosphere well W2NA (Tables 2 and 3). Presumably it is associated with wastes originally buried in these trenches. The hydrophilic organic fraction from waste trench 19S was much more complex than the counterpart for waste trench 27. An extensive variety of mono- and dicarboxylic acids and their oxygenated analogues was detected in waste trench 19S. In addition, EDTA-like organic species of varying molecular weights were identified in several samples for the first time. EDTA-like species, in the methylated form, of molecular weights 219, 244 and 288 were identified in water from waste trenches 27 and 19S. EDTA-like species of molecular weights 219 and 244 were also identified in water from inert atmosphere well W2NA. Possible structures that are consistent with the mass fragmentation patterns from GC-MS analysis are compared with EDTA in Figure 4.

The similarity between the mass spectra and proposed structures of these species and EDTA suggests that they arise from degradation of EDTA, perhaps resulting from microbial activity and from the influence of radioactive decay of buried waste. We have been unable to find man-made chelators with such molecular weights or mass spectra. The molecular weight 288 species was not observed in water from inert atmosphere well W2NA, suggesting that this

particular EDTA-like species is either labile or is preferentially retarded during subsurface migration. It is also possible that the 288 species may not be derived from EDTA and this is undergoing further scrutiny. Structural differences between EDTA and the other species are not great enough to suggest different sorption behavior. The absence of the molecular weight 288 species in the older waste trench 27 sample (4-7-81) combined with its presence in the newer waste trench 27 sample supports the assumption that the molecular weight 288 species, or its precursor if other than EDTA, is susceptible to degradation processes.

Several brominated organic species were detected in water from experimental trench sump S5 (Table 5). During construction of the experimental trench, sodium bromide was placed in the bottoms of sections one, two, three and five as a groundwater tracer. It seems likely, therefore, that the appearance of the brominated organic species in experimental trench section five is due to the bromination of polar organics present in the groundwater. Why these brominated species do not also appear in water from other sections of the experimental trench is more difficult to explain. However, we have observed that water inflow into section five is much slower than is observed for sections one, two and three. It is possible that the increased contact time between the sodium bromide tracer and stagnant groundwater in experimental trench section five has made possible the bromination of organic compounds in the groundwater.

The hydrophobic organic compounds were solvent extracted from the water samples to facilitate the chromatographic analyses of hydrophilic organic species, which include the radionuclide chelators. From these analyses we have also obtained preliminary information on toxic organic compounds that are present in waste trench waters and groundwater sampled from the experimental trench and inert atmosphere wells. In addition to the information on toxic compounds, which do not seem to be involved in the migration processes, it should also be possible to identify those compounds formed by bacterial degradation of buried waste. These latter compounds may have low to medium complexing strengths when compared with EDTA. We expect this study to help establish a basis for predicting long-term subsurface transport problems associated with radionuclide burial at shallow land burial sites.

In general, water samples from the experimental trench area contained few hydrophobic organic compounds. Some of the compounds, however (e.g. pyridine), are not typically found in uncontaminated soil samples. In contrast, the leachate from waste trench 27 contained quite a diversity of hydrophobic organics, possibly associated with waste dumped into the trench. Most of the hydrophobic organic compounds isolated from these water samples were present at parts-per-billion levels, and only three of these compounds were present at higher (i.e., parts-per-million) levels. These included pentafluorobenzoic acid (PFBA) and 2(3H)-benzothiazolone in waste trench 27 water (Table 6) and a group of alkylphenoxy oligomers primarily found in inert atmosphere well W2NA (Table 7).

PFBA was placed on the cap of experimental trench section 4 during construction of the experimental trench in 1979 (NUREG/CR-1832, pages III-10 and IX-6). The detection of PFBA in waste trench 27 water sampled in 1981 (1067

ppb) demonstrates that water movement had occurred from the area of experimental trench section 4 into waste trench 27 during the intervening time. Only a trace of PFBA was found in water from experimental trench section 4 during this same time frame, possibly due to infiltration by channeling along one of the sampler lines. The extremely low concentrations of PFBA in water from experimental trench section 4 suggests that there has been no appreciable penetration of this new trench cap and experimental trench section 4 was not the source of the PFBA measured in waste trench 27. PFBA probably entered waste trench 27 following surface runoff from the experimental trench area and subsequent infiltration into the waste trench.

Several heterocyclic compounds were identified among the hydrophobic species. The most abundant of these compounds is 2(3H)-benzothiazolone, which was present in waste trench 27 at 835 ppb. We are not acquainted with the uses of this compound, but the related compound benzothiazole, which was also present, is used industrially in the manufacture of rubber and appears in certain pesticides. The 2(3H)-benzothiazolone may be an oxidation or diagenesis product of benzothiazole, or it may be waste-derived. In addition, a variety of alkylphenoxy oligomers were measured in samples obtained in 1981, but are not present in the more recent waste trench samples. Such compounds are used as anionic detergents in applications where metallic ions (e.g., Na^+) are undesirable.

Many of the hydrophobic compounds are not typically found in uncontaminated water samples and some possess toxic properties. Two barbiturates, barbitol and pentobarbital, have been identified in water from waste trench 27 and inert atmosphere well W2NA. The two barbiturates are undoubtedly waste-related, presumably associated with biomedical waste. For example, pentobarbital is often used in pharmacological studies and barbitol has been commonly used as a buffering agent. Interestingly, the two barbiturates were identified only in older water samples from waste trench 27 (4/7/81) and inert atmosphere well W2NA (5/18/81). Their levels in these samples are real but quite low (ppb levels). Their absence in more recent water samples may be due to their depletion from the buried waste, causing their levels to fall below detection limits. Nevertheless, their appearance in water from inert atmosphere well W2NA, as well as the presence of EDTA in the same water samples, supports the concept of specific communication between waste trench 27 and inert atmosphere well W2NA. It should be noted that this communication is between locations only a few meters apart, and these compounds were not detected in other inert atmosphere wells about five to seven meters further away.

Radionuclide/Organic Compound Associations

Plutonium in waste trench 27 leachate is present in the reduced form as a strongly complexed anionic species (NUREG/CR-1832, page IV-8). To obtain evidence on the chemical behavior of plutonium complexes with complexing agents likely to be present in Maxey Flats trench waters, laboratory ion exchange experiments were performed with plutonium (+3) and plutonium (+4) and several candidate complexing agents (EDTA, TBP, TOA). Among the solutions studied, 10^{-6} M EDTA had the greatest effect on plutonium absorption. (The EDTA

concentration having the greatest effect on plutonium absorption in these experiments is nearly identical to the concentration measured in waste trench leachates.) The presence of a strong complexing agent like EDTA, even at these low concentrations, may actually be more important than the oxidation state of plutonium in determining whether it absorbs on a material with a high exchange capacity. These experiments support the view that plutonium is present in waste trench leachate as a strong complex, probably with EDTA (NUREG/CR-2383, page I-17).

In these studies we have continued to supplement our laboratory work with on-site chemical separations employing tracers and organic ligand separations. The on-site separations minimize solution degradation and thereby duplicate as closely as possible actual field conditions. We performed most of the preliminary analytical procedures in the field immediately following sample collection to guard against possible loss of organo-radionuclide complexes and chelates through sample degradation. For example, exposure to air will cause the precipitation of ferric hydroxide with an accompanying scavenging of radionuclide species. This condition becomes much more severe as the samples become more oxidic.

Field trips to perform in situ chemical separations of waste trench leachate and inert atmosphere well water samples at Maxey Flats to supplement our laboratory studies that are based on a monthly sampling frequency were conducted during the past year. Fractionated samples from these field trips have been undergoing detailed radionuclide and organic analyses to determine the precise chemical species present in each of the water sources. The ultraviolet chromatograms of the Sephadex-fractionated waters are reproduced in Figure 5. Each water sample exhibited a distinct chromatographic pattern, with the chromatograms from the two waste trench samples being much more complex than those from the inert atmosphere well samples. Based on the chromatograms, water from inert atmosphere well W2NA appears generally to contain lower molecular weight aggregates compared to the leachates from both waste trenches when samples are compared under the chromatographic conditions used in this study.

The detailed chemical speciation studies have demonstrated that EDTA is co-eluting with plutonium and ^{60}Co during steric exclusion chromatography of water from waste trenches 27 and 19S and inert atmosphere well W2NA. Strontium-90 and ^{137}Cs also appear to be associated with polar organic compounds, notably palmitic (hexadecanoic) and stearic (octadecanoic) acids, suggesting that some form of salt-like complexation exists for these radionuclides. Quantitation of EDTA and of radionuclides in the concentrated and fractionated samples has demonstrated that the soluble plutonium is associated with EDTA.

Some of the plutonium originally present in the water samples is removed from the water during concentration of the samples by co-precipitation with iron. This occurs due to exposure to traces of oxygen or because the solubility limits for iron have been exceeded in the concentrated samples. This observation suggests that uncomplexed plutonium will be fixed to the soil with the iron hydroxide precipitate when the anoxic groundwater is exposed to oxidizing conditions.

SUBSURFACE MIGRATION AND INFILTRATION STUDIES

The experimental trench and wells study was undertaken to determine if subsurface migration of radionuclides had occurred at Maxey Flats, to measure the extent of any such migration, and to define the processes by which movement occurs. The work is continuing to utilize the experimental installations we established on the Maxey Flats site (see Figure 1) for defining migration rates and specific chemical species of long-lived fission products and the trans-uranium elements. It is also allowing the determination of the chemical species of migrating nonradioactive elements associated with waste and utilizes non-radioactive tracer movement to evaluate the effects of engineered trench caps and drainage systems on water infiltration rates.

Sampling frequency considerations summarized by Loftis and Ward (1980) to delineate the roles of serial correlation and seasonal variation are employed in these studies. During the past year, we have continued sampling the experimental trench sumps and inert atmosphere wells (Figure 2) on a monthly frequency, weather and water levels permitting, and analysis of the samples for radionuclides and organic compounds is continuing. The water samples are analyzed for ^3H , gamma-ray emitting radionuclides (e.g., ^{60}Co , ^{137}Cs), alpha particle emitting radionuclides (e.g., ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Am), hydrophilic and hydrophobic organic species, and nonradioactive elements that can be determined by neutron activation (e.g., Br). These measurements verify that within the Maxey Flats restricted area subsurface migration of radionuclides has occurred over limited distances (NUREG/CR-2383, page I-13). Except for tritium, migration to points outside the restricted area has not been a significant source of contamination by radionuclides.

Water samples collected during the reporting period have undergone analysis at PNL during the past year. We have also begun sampling several of the E-series wells (Figure 6) at Maxey Flats to obtain information on any radionuclides which migrate for significant distances and also provide information on the utility of such a set of wells for monitoring site performance following closure. Wells E-5, E-12 and E-13 were selected for sampling. Water samples are being composited to obtain the large volumes of water needed to measure the low concentrations of radionuclides that are expected to be present. We plan to composite samples collected over several months and perform radionuclide separations on the composited samples using the techniques developed for large volume water sampling (Silker 1971). These samples will provide information on any radionuclides which migrate for significant distances and also provide information on the utility of such a set of wells for monitoring site performance following closure.

The decision to construct an experimental trench was based on the premise that this design offered the best opportunity to intercept subsurface flow from waste trenches, either through fracture flow at sandstone-shale interfaces, or through direct flow. Indeed, water that may not have been intercepted by wells flowed into three sections of the experimental trench during

construction. The initial radioactive concentrations were comparable to waste trench 27 leachate, as shown in Table 10. The radionuclide concentrations measured in these construction samples clearly show that subsurface movement of radionuclides has occurred at Maxey Flats, but the distance of migration cannot be inferred from these data.

When the experimental trench was resampled on later dates, most radionuclide concentrations showed marked decreases, suggesting that the radionuclides were present initially only in the experimental trench location due to a decrease of hydraulic pressure during construction that permitted flow to occur from the waste trench into the experimental trench area. However, it is also possible that the trench design had adversely influenced the concentrations of radionuclides in water flowing toward the trench sumps through changes in the water chemistry. The exposure of the open trench to air during construction resulted in the formation of an in-place scavenger (ferric hydroxide), which reacted synergistically with the crushed rock backfill to form an absorptive barrier for radionuclide transport. Consequently, the decision was made to install monitoring walls in undisturbed soil near the experimental trench to collect anoxic samples for chemical species determinations (Figure 2).

Water flowed into six of the inert atmosphere sampling wells during the post-construction period. Radionuclide and bromine concentrations from these wells are compared with waste trench leachate in Table 11. Changes in bromine concentrations that have been observed in waste trench 27 leachate since 1978 and in water from the experimental trench and inert atmosphere wells indicate that there is some communication by groundwater flow between these locations. These comparisons are made possible in part by the presence of sodium bromide (NaBr) tracer added to sections 1, 2, 3 and 5 of the experimental trench during its construction in 1979. Bromine concentrations in waste trench 27 leachate were quite low prior to the construction of the experimental trench. Following trench construction, the bromine concentration in waste trench 27 increased from 2.8 to 460 ppm, indicating that some of the NaBr tracer had moved into waste trench 27. The well point samples had low concentrations of bromine, probably because the well point was installed opposite section 4 of the experimental trench, which contains no added water. There seems to be no direct communication by groundwater flow between section 4 and the well point.

Bromine concentrations in the inert atmosphere wells could also be influenced by the presence of NaBr in sections 1, 2 and 3 of the experimental trench. Wells W3N and W3NA show this influence even more markedly than the comparison with waste trench 27, since the wells are much closer to the NaBr source. Well W2NA also indicates a communication with the NaBr source while wells W1N, W2N and W5N seem not to be connected to the NaBr source. When radionuclide concentrations are compared, only W2NA and W3N appear to be closely related to waste trench 27, possibly connecting to it through subsurface fractures.

The tritium concentrations in samples from trench sections T2 and T3 have shown very marked decreases since the experimental trench was constructed, indicating that there is substantial movement of water away from the trench in

this region. The tritium concentration in waste trench 27 leachate has been relatively stable during the same time; the waste trench leachate apparently did not flow toward the experimental trench to maintain the tritium concentrations near the levels that were originally observed in sections T2 and T3. It is unlikely that this degree of dilution could have come from water filtering through the trench caps, since only one of the nonradioactive tracers installed in these caps was detected in trace quantity in section 4 of the experimental trench. The tritium data, as do the bromine data, show that some water flow has occurred away from the experimental trench and toward waste trench 27 during the study period. Water from sections T2 and T3 would therefore be diluted by subsurface lateral flow of low-tritium water moving from the south toward the experimental trench.

The complexity of groundwater flow in the experimental trench area is summarized in Figure 7. Data from five sources seem to indicate basically different flow directions. However, these directions would be dependent upon characteristics existing at the time of the measurements. They certainly would be influenced by infiltration of surface runoff water and by pumping of leachate (especially from waste trench 27) to the evaporator. The data summarized in Figure 7 were obtained prior to the installation of the flexible vinyl infiltration barrier over the burial area, and during a time of intense evaporator use. Immediately after the shutdown of the evaporator and cessation of pumping at the end of 1982, tritium concentrations increased dramatically in the wells farthest south from waste trench 27 (W1S, W2S and W3S), indicating that major changes in groundwater flow were occurring. This occurred primarily because the trench leachates were no longer being pumped to the evaporator and infiltration of surface runoff water was prevented by the installation of the flexible vinyl infiltration barrier over the burial area. Following this initial rapid change over a two-month period, water levels and radionuclide concentrations have once again begun to exhibit little further change, indicating that the groundwater table has stabilized.

SPECIFIC RADIONUCLIDE MAPPING AT MAXEY FLATS AND OTHER COMMERCIAL SHALLOW LAND BURIAL SITES

The Maxey Flats burial site has been contaminated by several sources. These include the overflow of water from the burial trenches as rainwater infiltrated and filled them, spillage during pumping of excess water from the trenches, fallout from entrained radionuclides in the evaporator plume, and surface runoff of radioactive solutions from the site. To obtain a better understanding of the actual sources of radioactivity in surface soils and vegetation on the burial sites and adjacent areas, a detailed study of the levels of radioactivity has been performed at Maxey Flats and related studies should also be useful at other commercial shallow land burial sites.

In situ gamma ray surveys conducted at the Beatty, Nevada (NUREG/CR-1524), and Maxey Flats, Kentucky (NUREG/CR-2383, Section II and NUREG/CR-1832, Section IV) shallow land burial sites confirmed that most of the waste radionuclides have been retained within the boundaries of those sites. The in situ measurements were correlated with and augmented by analysis of samples taken from

each of the counting locations, since only the more energetic gamma ray emitting radionuclides are measured by the in situ procedures.

Two general kinds of radionuclides were determined in these studies. They are endogenous (natural) radionuclides originating from the parent soil material and exogenous (man-induced) radionuclides originating from the nuclear fuel process. Cobalt-60 and ^{137}Cs are exogenous radionuclides and both are constituents of global fallout as well as being components of low level radioactive wastes stored at Maxey Flats. Potassium-40 and ^{228}Th are endogenous radionuclides originating from the underlying rock strata and soil. In a typical gamma-ray spectrum, most of the peaks are due to endogenous radionuclides, chiefly natural uranium, thorium, and their daughters, plus ^{40}K (Figure 8).

Very low concentrations of radionuclides were present in most soil samples. Cesium-137 and ^{60}Co were the most abundant radionuclides of exogenous origin and these have their origin in global fallout, which is ubiquitously distributed over all land surfaces. The distribution of ^{60}Co in surface soils within and adjacent to the restricted area at Maxey Flats in May, 1980 is plotted in Figure 9. The data have been separated into three levels of ^{60}Co soil concentrations -- greater than 2 pCi ^{60}Co per gram of soil, 1-2 pCi ^{60}Co per gram of soil, and less than 1 pCi ^{60}Co per gram of soil. A similar plot for ^{137}Cs distribution in surface soils within and adjacent to the restricted area at Maxey Flats is shown in Figure 10.

In general, a distribution pattern for any one radionuclide may not be used to predict a distribution pattern for another radionuclide, except in those instances relating to the purely endogenous radionuclides originating from the parent soil material. Even these latter distributions may be skewed by the presence of specific processing wastes from thorium or uranium purification processes because of the introduction of nonequilibrium quantities of their daughters from the decay chains.

The soil in the west drainage channel leading from the restricted area contains surface concentrations of ^{60}Co that exceed the background fallout levels away from the site. Virtually all of the ^{60}Co is contained in the first few centimeters of soil and all counts made downhill more than 100 meters from the site showed the ^{60}Co concentration to be at the fallout level measured at background locations away from the site (less than 0.1 pCi ^{60}Co per gram of soil). In the south and east drainage channels ^{60}Co concentrations within the drainages are at the background levels. Cesium-137 concentrations in surface soil within the restricted area and in the main drainage channels leading from the site are similar to concentrations found in other locations of the United States that have rainfall patterns like those of eastern Kentucky. Although it is apparent that surface runoff from the site could contribute ^{137}Cs to the adjacent drainages, in situ measurements and soil sample analyses indicate that ^{137}Cs is not derived from the Maxey Flats site.

These studies have demonstrated that surface contamination by radionuclides has been retained mainly within the restricted area at Maxey Flats. Surface sediments in areas adjacent to the site, primarily on the west side,

contain ^{60}Co in concentrations greater than fallout. The origin of the ^{60}Co is from surface runoff into the adjacent woods. Measurements made to date indicate that offsite contamination has not resulted from subsurface transport, except possibly for tritium. The relative contributions of tritium from air (evaporator output), surface and subsurface pathways are still being evaluated. These comparisons are possible because of the installation of vinyl cover over the burial trenches and the shutdown of the evaporator for an extended period of time, allowing the full impact to be determined.

ECOLOGICAL MONITORING AT COMMERCIAL SHALLOW LAND BURIAL SITES

In this task we are developing efficient and statistically valid ecological field sampling procedures and methods for post-closure monitoring at commercial shallow land burial sites. Kinds and amounts of radionuclides and trace elements in environmental samples are being measured with emphasis on biotic uptake, bioaccumulation, biotic transport, and ecological pathways in semi-wild ecosystems. We are emphasizing the sampling for pattern approach to provide three dimensional data that are amenable to rigid statistical analysis.

Several possible migration pathways exist for radionuclides buried at the Maxey Flats shallow land burial site. To evaluate potential biotic pathways, forest floor litter, newly fallen leaves, newly opened leaves and surface soil were sampled in the forest surrounding the restricted area and analyzed by high resolution gamma-ray spectroscopy. Most of the radionuclides in the forest were associated with the soil, with relatively small amounts of radionuclides associated with the litter and leaves. The endogenous radionuclides ^{40}K and ^{228}Th dominated soil distributions, but the exogenous radionuclides ^{60}Co and ^{137}Cs were relatively more abundant in the litter layer. The ^{60}Co content of newly fallen leaves (Figure 11) was more variable than the other radionuclides, suggesting that the burial site has influenced the ^{60}Co concentrations at a few sampling locations and newly opened leaves from one hickory tree suggested that the source of the elevated ^{60}Co concentrations was the rooting substrate. The other radionuclide concentrations exhibited little variation between tree species from location to location.

During the past year, autumn leaf-fall samples were collected from the 0.5 m^2 rectangular wire baskets placed beneath the permanently tagged trees adjacent to the Maxey Flats restricted area. These samples have been dried and shipped to our PNL facilities at Richland, Washington, where they are undergoing analysis by gamma-ray spectrometry. We expect to determine the exogenous radionuclides (e.g., ^{60}Co , ^{137}Cs) and at the same time will obtain information on endogeneous (e.g., ^7Be , ^{40}K , ^{226}Ra , ^{228}Th) radionuclides and compare their concentrations with values reported from earlier sampling runs (NUREG/CR-2383, Section III, and NUREG/CR-1832, Section V).

Leaf sampling from living trees was conducted to determine tritium distributions adjacent to the Maxey Flats facility in July, 1982. With the exception of two maple trees sampled in the west drainage channel, the leaf samples were taken from large oak trees. Leaf water was subsequently purified and analyzed

for tritium and the data compared with similar scouting measurements conducted in 1981. The data are summarized in Figure 12. Data from the measurements conducted on the west side of the restricted area are displayed on a contour map in Figure 13. These data indicate that there are no major tritium sources originating from seepage at the lower elevations leading from the site. If there were major seeps one would expect to see local elevated levels of tritium down the hill, which is not the case. These data show a slight peaking in trees sampled adjacent to the site near waste trenches 30 and 31. Trench 31 has a high inventory of buried tritium, which is contained in drums which are packed with an absorbing agent. If there were to be drastically higher concentrations of tritium in three trees near this trench, it would have to be explained on the basis of sub-surface groundwater flow from that trench. The absence of these drastically elevated levels shows that there is probably very little subsurface flow from trench 31 to the adjoining unrestricted area. Additional study is needed here to determine whether any tritium migration is actually occurring. The data thus far indicate that the tritium levels around the site have been controlled by condensation from the evaporator plume. Additional leaf sampling conducted during October 1982 demonstrated that there are no obvious seasonal fluctuations for tritium in trees.

Leaf water data indicate that tritium in above ambient fallout levels has migrated into the edge of the forest at Maxey Flats. Maple trees, Acer sacharum, also have the unusual ability to move water through their trunk before new leaves emerge in the spring. If maple tree roots have access to tritiated water, tritium will appear in the sap stream. Experience at Maxey Flats indicates that sap samples for tritium analyses can be obtained by tapping tree trunks in a cost-effective and a biologically nondestructive fashion useful for post-closure ecological monitoring programs. Sampling trips were made to Maxey Flats during March, 1983 to collect sap from maple trees for tritium analyses. These trips were scheduled to correspond with the season of most vigorous sap flow. Maple trees were tapped at more than 50 locations around the Maxey Flats disposal site (Figure 14) and two trees were tapped at a control location in a similar forest type near Cave Run Lake, about 12 miles south of Maxey Flats. The results of preliminary tritium analyses are presented in Figure 15. Tritium concentrations ranged from below detection level to 290,000 pCi per liter of tree sap with the highest values observed in two trees located along the western side of the disposal site. In general, tritium values declined with increasing distance from the disposal site. The lowest values were measured near Cave Run Lake and these values represent fallout (background) tritium levels.

The analyses of tree sap and water from transpiring leaves indicate that tritium uptake by deep-rooted trees has potential to serve as a biomonitor of subsurface movement of water from burial sites. Tree sampling is inherently much less expensive than well drilling and may be a way to detect groundwater contamination in the upper 10-15 meters of soil. Trees offer an advantage over wells because the roots sample a larger volume of rock than a well and in fractured impermeable media such as exists at Maxey Flats tree roots will actively seek out water. Wells in such a situation may miss major bearing fractures by a few centimeters and will not be effective in sampling water in these

fractures. These surveys have indicated that biomonitors may be very useful as indicators of radionuclide migration from shallow land burial sites. Tritium is environmentally one of the most mobile of radionuclides and it can move as tritiated water, as vapor, or in surface or groundwater flows. Trees obtain water from their rooting substrate and move it from roots to stems to leaves, and release water to air as vapor. Water can be extracted from fresh tree leaves and analyzed for tritium. If tritium is present in the root zone, it appears in the extracted water. Because trees have deeply penetrating roots, as compared to crop plants, they can be used to monitor subsurface water flows.

Ecological field sampling performed at Maxey Flats has concentrated on the detection of gamma-emitting radionuclides and tritium in the semi-wild forest surrounding the disposal facility. Although a broad spectrum of naturally-occurring and fallout-derived radionuclides has been measured in leaves, forest floor litter and surface soil, only ^3H and ^{60}Co are elevated above ambient fallout levels and appear to originate from the disposal site. Even these radionuclides are at only slightly elevated levels - well below the MPC's for drinking water. Other radionuclides are naturally occurring or are constituents of global fallout. These surveys indicate that leaf fall, leaf sampling and sap sampling can be cost-effective and nondestructive sampling procedures that can be incorporated into ecological monitoring programs to indicate migration or lack of migration from shallow land burial sites.

Carbon-14 is present in the waste trenches at Maxey Flats and is one of the radionuclides of concern for ecological monitoring following site closure (10 CFR 61). Although ^{14}C has been widely used as a tracer in biological experiments, comparatively little is known about the root uptake of ^{14}C from soil or soil water. In recent experiments, wood samples from borings in tree trunks and also from twigs produced in the 1982 growing season were taken from four trees near the fence line of the restricted area at Maxey Flats. One tree was sampled at Cave Run Lake, about twelve miles south of the site. These samples are currently undergoing analysis for ^{14}C to determine whether ^{14}C has the potential for migration and uptake by deep-rooted trees.

TECHNICAL PROGRAM COORDINATION FOR LOW-LEVEL WASTE RESEARCH

PNL assisted in the preparation of the agenda for an annual review of policy and research progress of NRC research at the Maxey Flats LLW disposal site. This meeting was held October 26-28, 1982 at the Natural Bridge State Park, Slade, Kentucky, and at the Maxey Flats site. Participants included representatives of NRC's offices of Nuclear Regulatory Research, Nuclear Material Safety and Safeguards and State Programs. Other participants included representatives of PNL, LANL, UCB, BNL, USGS, the Commonwealth of Kentucky, Hittman Nuclear and Development Co., Illinois Geological Survey, Morehead State University and Oak Ridge National Laboratory.

A tour of the Maxey Flats site was conducted to acquaint all participants with the physical features of the site, the present on-site operations, and the on-site experimental installations of the various contractors. This was followed by a summary review of the current state of knowledge concerning the

site, a review of the NRC contractors' research projects, and discussions of problem areas and further research needs for bringing about a closure of the site. An informal summary report was distributed to the attendees.

PNL assisted in the preparation of the agenda for discussions of research observations at Maxey Flats which are relevant to site closure. This meeting was held November 30 and December 1, 1982 at USGS offices in Reston, Virginia. Participants included representatives of NRC's offices in Reston, Virginia. Participants included representatives of NRC's offices of Nuclear Regulatory Research, Nuclear Material Safety and Safeguards and State Programs. Other participants included representatives of PNL, LANL, UCB, BNL, USGS and the Commonwealth of Kentucky. An informal report, "Initial Review of Research Observations at Maxey Flats which are Relevant to Site Closure" has been distributed to panel members, including representatives of NRC's offices of Nuclear Regulatory Research, Nuclear Material Safety and Safeguards, and State Programs. Other panel members included representatives of PNL, LANL, UCB, BNL, USGS and the Commonwealth of Kentucky.

TECHNICAL PROGRAM COORDINATION FOR LOW-LEVEL WASTE RESEARCH

PNL assisted in the preparation of the agenda for an annual review of policy and research progress of NRC research at the Maxey Flats LLW disposal site. This meeting was held October 26-28, 1982 at the Natural Bridge State Park, State of Kentucky, and at the Maxey Flats site. Participants included representatives of NRC's offices of Nuclear Regulatory Research, Nuclear Material Safety and Safeguards and State Programs. Other participants included representatives of PNL, LANL, UCB, BNL, USGS, the Commonwealth of Kentucky, Western Nuclear and Development Co., Illinois Geological Survey, Morehead State University and Oak Ridge National Laboratory.

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FIGURE 1. Maxey Flats waste trenches and experimental areas. The numbered lines show the approximate locations of the waste trenches. Experimental area number 1 includes the experimental trench (T1 through T5) and inert atmosphere wells (open circles). Experimental area number 2 includes the porous cup and tensiometer installations for studying water movement into trenches and water and radionuclide movement out of trenches. Experimental area number 3 includes the UCB lysimeter installations for water balance studies. These experimental areas support research studies by PNL, LANL, UCB and BNL.

FIGURE 2. Maxey Flats experimental area No. 1, containing the experimental trench and wells near waste trench 27. These facilities allow concurrent sampling of the experimental trench, inert atmosphere wells and adjoining waste trench for PNL groundwater migration and chemical species studies. The experimental trench is also used by LANL, UCB, and BNL in research studies at the Maxey Flats Shallow Land Burial Site.

FIGURE 3. Groundwater Analysis Sequence

FIGURE 4. Possible structures of methylated EDTA degradation products are compared with EDTA-Tetramethyl ester. The structures are based on mass fragmentation patterns from GC-MS analysis. The EDTA-like structures of molecular weights 219, 244 and 288 were present in water from waste trenches 27 and 19S, as was EDTA. The EDTA-like structures of molecular weights 219 and 244 were present in water from inert atmosphere well W2NA, as was EDTA. Samples were collected at Maxey Flats, Kentucky, July, 1982.

Figure 5. Steric exclusion chromatography of waste trench leachate and inert atmosphere well water samples at Maxey Falls, sampled July, 1982. Organic compounds were separated by size and individual fractions were analyzed for specific organic compounds and radionuclides. EDTA is the main organic compound in three of the samples and co-eluted with alpha-emitting radionuclides and ^{60}Co . Strontium-90 and ^{137}Cs coeluted with polar organic compounds.

FIGURE 6. Relative locations of the E-series wells around the Maxey Flats restricted area. Wells 5E, 12E and 13E were chosen for large volume sampling to provide information on any radionuclides which migrate for significant distances and provide information on the utility of such a set of wells for monitoring site performance following closure.

FIGURE 7. Groundwater flow patterns within experimental area No. 1 at the Maxey Flats Disposal Facility. Data from five sets of measurements indicate basically different underground flow directions which have been influenced by construction activities, infiltration of surface water and by pumping activities while the evaporator was operating.

FIGURE 8. Typical in situ gamma-ray spectrum at Maxey Flats, Kentucky. Most of the gamma-ray peaks observed are due to endogenous radionuclides originating from the parent soil material. In the example above, the exogenous radionuclides ^{60}Co and ^{137}Cs are also present in low concentrations.

FIGURE 9. Cobalt-60 distribution in surface soil within and adjacent to the restricted area at Maxey Flats (May, 1980). Areas within the solid isopleths have ^{60}Co concentrations > 2 pCi per gram of soil. Areas within the dotted isopleths have ^{60}Co concentrations 1-2 pCi per gram of soil. All other areas on site have ^{60}Co concentrations < 1 pCi per gram of soil.

FIGURE 10. Cesium-137 distribution in surface soil within and adjacent to the restricted area at Maxey Flats (May, 1980). Areas within the solid isopleths have ^{137}Cs concentrations > 2 pCi per gram of soil. Areas within the dotted isopleths have ^{137}Cs concentrations 1-2 pCi per gram of soil. All other areas on site have ^{137}Cs concentrations < 1 pCi per gram of soil.

FIGURE 11. Potassium-40, ^{137}Cs and ^{60}Co in newly fallen leaves in the oak-hickory forest at Maxey Flats, Kentucky. Whereas most ^{137}Cs and ^{60}Co concentrations are at fallout levels, the ^{60}Co concentrations at locations 13 & 14 are probably not directly attributable to fallout.

FIGURE 12. Tritium concentrations in systemic water from trees adjacent to the Maxey Flats site in July, 1981 and July, 1982. Concentration units are 10⁴ pCi/l. Tritium concentrations measured in 1982 (unbracketed numbers) are about ten-fold lower than corresponding 1981 data (bracketed numbers) along the fence line bordering waste trenches 27-32, 41, 35 and 36. All concentrations are well below MPC.

FIGURE 13. Tritium concentrations in systemic water from trees in the west drainage at Maxey Flats in July, 1981 (bracketed numbers) and July, 1982 (unbracketed numbers). Concentration units are 10^4 pCi/l and contour intervals are in feet. The absence of any drastically elevated tritium levels at the illustrated elevations demonstrates that there is probably very little subsurface flow from the site.

FIGURE 14. Locations of sap sampling trees (•) near the Maxey Flats site, 1983. Individual maple trees were sampled and the sap was analyzed for tritium. Concentrations range from a low value of <430 pCi/l at a location about 12 miles south of the site to a high value of 2.9×10^5 pCi/l at a location near the west side of the site. Tritium concentrations decreased rapidly with distance from the site. All concentrations are well below the MPC for tritium in drinking water.

FIGURE 15. Tritium distributions at the Maxey Flats Disposal Facility, March, 1983. The concentration ranges of tritium in leaf water are indicated by the numbered regions between the curved lines overlaying the site boundaries. Concentration isopleths were derived for median block values by Kriging the tritium concentrations determined in maple sap collected within the indicated area.

TABLE 1. Maxey Flats Experimental Trench Summary

	Trench Section				
	T-1	T-2	T-3	T-4	T-5
Gamma-Ray Logging	Partial	Yes	-	Yes	-
Geologic Logging*	-	Partial	-	-	-
Water In-Flow	Yes	Yes	Yes	-	-
Sumps	2	2	2	1	1
Porous Cups in Trench Wall	-	-	-	Three Vertical Traverses + Cap	-
Soil Moisture Cells in Trench Wall	-	-	-	One Vertical Traverse + Cap	-
Cap Design	Local Soil/ Clay	Local Soil/ Clay	Local Soil/ Mirafi-140/ Clay	Local Soil/ Clay	Clay/ Hypalon/ Clay
Groundwater Tracer	NaBr	NaBr	NaBr	-	NaBr
Cap Tracers	Na Benzoate	o-Fluoro- benzoic Acid	Na Benzoate	Pentafluoro- benzoic Acid	Na Benzoate
Root Penetration Tracers	BaCl ₂ NiSO ₄	Sr(NO ₃) ₂ Li ₂ CO ₃			
Vegetation Plots	Yes	Yes			
Drainage Ditches	Drain Trench Cap for Tracer Studies and Erosion Control				

*Limited by safety considerations.

TABLE 2. Hydrophilic Organic Compounds^a in Waste Trench Leachate

	Concentration (ppb) ^b in Water Samples (See Figure 1 for Sampling Locations)		
	Waste Trench 27 (4/7/81)	Waste Trench 27 (7/27/82)	Waste Trench 19S (7/22/82)
Ethylenediaminetetraacetic Acid (EDTA) ^d	1000	3830	1340
EDTA Fragment ^d (MW 288)		90	88
EDTA Fragment ^d (MW 244)	145	758	259
EDTA Fragment ^d (MW 219)	Trace	Trace	
Citric Acid ^d	8	Trace	
Succinic Acid ^d	23		29
Methyl Succinic Acid ^d	Trace		
Hexanedioic Acid ^d	26	45	71
Nonanedioic Acid ^d	20		192
Nonanoic Acid ^d		Trace	
Dodecanoic Acid ^d		1	
Hexadecanoic ^d	28	267	
Octadecanoic Acid ^d	32	26	
4-oxo-pentanoic Acid ^d	19		76
Oxalic Acid ^d	28		35
Benzoic Acid ^d	1		200
Pentafluorobenzoic Acid ^{d,e}	Trace		
Dimethyl Phthalate	90	26	558
Dibutyl Phthalate	68	51	
Diethyl Phthalate	36	2	4
Silicone Oil Oligomers	67		

a. Methylated, BF₃/Methanol

b. No entry indicates compound is below detection level

c. Multiple sampling dates

d. Methyl Ester

e. Groundwater tracer added to the cap on experimental trench section four

Note: The data reproduced here demonstrate that EDTA is the major organic complexing agent in water from waste trench 27 and waste trench 19S, and several other organic acids (carboxylic acids) are present. Both types of compound appear to influence radionuclide migration within the Maxey Flats site.

TABLE 3. Hydrophilic Organic Compounds^a in Inert Atmosphere Well W2NA

	Concentration (ppb) ^b in Water Samples ^c (See Figure 2 for Sampling Locations)		
	5/18/81	8/17/81	6/14/82
Ethylenediaminetetraacetic Acid (EDTA) ^d	1088	1009	793
EDTA Fragment ^d (MW 244)	125	145	171
EDTA Fragment ^d (MW 219)	Trace	Trace	Trace
Citric Acid ^d	Trace	18	
Oxalic Acid ^d	61	67	
Succinic Acid ^d		41	
Methyl Succinic Acid ^d	7		
Propanedioic Acid ^d	1		
Butanedioic Acid ^d	20	14	
Hexanedioic Acid ^d	9	8	
Octanedioic Acid ^d		4	
Nonanedioic Acid ^d	17	33	Trace
Nonanoic Acid ^d		Trace	
Tridecanedioic Acid ^d	15	18	
Hexadecanoic Acid ^d	58	14	15
Octadecanoic Acid ^d	111	16	51
4-oxo-pentanoic Acid ^d	48	92	
Lactic Acid ^d		52	
Phenoxyacetic Acid ^d	123		
Benzoic Acid ^d	78	21	Trace
Dimethyl Phthalate	115	14	13
Dibutyl Phthalate	17	28	51
Diethyl Phthalate		13	2
Dimethyl Sulfate		33	

a. Methylated, BF₃/Methanol

b. No entry indicates compound is below detection level

c. Multiple sampling dates

d. Methyl Ester

Note: The data reproduced here demonstrate that EDTA is the major organic complexing agent in water from well W2NA. The data show several similarities to data in Table 1, indicating rather specific communication between waste trench 27 and inert atmosphere well W2NA.

TABLE 4. Hydrophilic Organic Compounds^a
in Inert Atmosphere Wells

	Concentration (ppb) ^b in Water Samples (See Figure 2 for Sampling Locations)			
	W1NC 8/17/81	7/26/82	W2M 8/17/81	W2MA 8/17/81
Citric Acid ^d			10	1
Oxalic Acid ^d	1		10	3
Succinic Acid	1	1	16	2
Methyl Succinic Acid ^d			10	2
Propanedioic Acid ^d			8	1
Pentanedioic Acid ^d			3	1
Hexanedioic Acid	1	1	43	8
Nonanedioic Acid ^d	1	2	8	1
Hexanoic Acid ^d	1			
Octanoic Acid ^d	2	1		
Nonanoic Acid ^d	3	2	Trace	
Decanoic Acid ^d	2	2		
Dodecanoic Acid ^d		2	2	
Tridecanedioic Acid ^d			14	
Tetradecanoic Acid ^d	2	3	1	
Hexadecanoic Acid ^d	8	7	8	4
Octadecanoic Acid ^d	6	4	8	3
4-oxo-pentanoic Acid ^d	2	3	3	15
Lactic Acid ^d	2			
Benzoic Acid ^d	2	1	5	4
Dimethyl Phthalate	2	4	13	3
Dibutyl Phthalate	6	10	7	4
Diethyl Phthalate	5	3	4	4
Dimethyl Sulfate		Trace	14	11
Silicone Oil Oligomers			33	7

a. Methylated, BF₃/Methanol

b. No entry indicates compound is below detection level

c. Multiple sampling dates

d. Methyl Ester

Note: The data reproduced here demonstrate that the wells above do not have the specific communication with waste trench 27 that is exhibited by well W2MA. Note for example, that EDTA and EDTA-like fragments were not detected in the wells above.

TABLE 5. Hydrophilic Organic Compounds^a
in Experimental Trench Sumps

	Concentration (ppb) ^b in Water Samples (See Figure 2 for Sampling Locations)	
	Sump S4 8/18/81	Sump S5 8/18/81
Oxalic Acid ^c		4
Succinic Acid ^c	2	4
Hexanedioic Acid ^c	17	8
Nonanedioic Acid ^c	14	
Tridecanedioic Acid ^c		13
Nonanoic Acid ^c		7
Tetradecanoic Acid ^c		10
Hexadecanoic Acid ^c	16	41
Octadecanoic Acid ^c	11	26
4-oxo-pentanoic Acid ^c	28	7
Lactic Acid ^c		4
Benzoic Acid ^c	7	6
Pentafluorobenzoic Acid ^c	Trace	
Dimethyl Phthalate	52	
Dibutyl Phthalate	9	14
Diethyl Phthalate	23	14
Dimethyl Sulfate	7	
Brominated Organics		d

a. Methylated, BF₃/Methanol

b. No entry indicates compound is below detection level

c. Methyl Ester

d. Not quantified

Note: The data reproduced here when compared with the data in Table 1 demonstrate that there is very little specific communication between experimental trench sections 4 and 5 and waste trench 27.

TABLE 6. Hydrophobic Organic Compounds
in Waste Trench Leachate

	Concentration (ppb) ^a in Water Samples (See Figure 1 for Sampling Locations)		
	Waste Trench 27		Waste Trench 195
	(4/7/81)	(7/27/82)	(7/22/82)
Pentafluorobenzoic Acid	1067		
Barbital	6	1	
Pentobarbital	2	1	
Piperidinone		0.2	0.5
Methyl Methacrylate	2		
Caprolactam		0.3	
1,3-dihydro-2H-Indol-2-one	6		
Methyl Butenone	9		
Dichloriodomethane	4	0.2	
Bromodichloromethane	3	0.7	0.2
Dichloromethylbutane	2		
Chloromethylbutene	10		
Toluene	23		
Benzofuran	10		
Benzothiazole	13		
Benzotriazole	3	Trace	
2(3H)-benzothiazolone	835	8	
C ₂ -toluenesulfonamide	1	1	1
C ₃ -toluenesulfonamide	0.1		
2,5-dimethyl Benzene Butanoic Acid	17		
Phthalic Anhydride	17		
Undecane	3		
Dodecane	4		
Tridecane	3		
Alkanes (C ₂₀ -C ₃₁)	197		
Alkylphenoxy Oligomers	102		

a. No entry indicates compound is below detection level

Note: Most of the hydrophobic compounds are not typically found in uncontaminated groundwaters and are probably waste-derived. A few compounds (e.g., barbital and pentobarbital) are also found in inert atmosphere well W2NA (Table 6), indicating communication with waste trench 27. The groundwater tracer pentafluorobenzoic acid added to the cap of experimental trench section four probably entered waste trench 27 following surface runoff from the experimental trench area and subsequent infiltration into the waste trench.

TABLE 7. Hydrophobic Organic Compounds
in Inert Atmosphere Well W2NA

	Concentration (ppb) ^a in Water Samples ^b (See Figure 2 for Sampling Locations)		
	5/18/81	8/17/81	6/14/82
Barbital	2		Trace
Pentobarbital	1		0.2
Nicotine	2		
Methyl Butenone	99		
Dichloriodomethane	6		0.2
Bromodichloromethane	0.7		1
Dichloromethylbutane	38	3	
Chloromethylbutene	107	21	
Toluene	64		
Benzofuran	16		
Alkylphenoxy Oligomers	963	Trace	

a. No entry indicates compound is below detection level.

b. Multiple sampling dates.

Note: Two of the compounds, barbital and pentobarbital, are present in well W2NA because of specific communication with waste trench 27. The group of alkylphenoxy oligomers is probably derived from the past use of anionic detergents. These compounds were also present in earlier water samples (collected 1981) from other wells and from waste trench 27.

**TABLE 8. Hydrophobic Organic Compounds
in Inert Atmosphere Wells**

	Concentration (ppb) ^a in Water Samples (See Figure 2 for Sampling Locations)			
	W1NB 8/17/81	7/26/82	W3N 8/17/81	W3NA 8/17/81
Pyridine	97			
Nicotine			4	
Methyl Methacrylate	9			
Methyl Butenone			21	
Bromodichloromethane	0.3	Trace		0.6
Dichloromethylbutane	7		21	36
Chloromethylbutene	20		57	94
Toluene			92	72
Benzofuran			42	37
C2-toluenesulfonamide	Trace			
N,N-bis(phenylmethyl)amine	3			4
Undecane			27	15
Dodecane			19	19
Tridecane			17	18
Alkanes(C20-C31)	9			158
Alkylphenoxy Oligomers	197		1144	735

a. No entry indicates compound is below detection level.
b. Multiple sampling dates.

Note: The group of alkylphenoxy oligomers is probably derived from the past use of anionic detergents. These compounds were also present in earlier water samples (collected 1981) from well W2NA and from waste trench 27.

**TABLE 9. Hydrophobic Organic Compounds
in Experimental Trench Sumps**

	Concentration (ppb) ^a in Water Samples (See Figure 2 for Sampling Locations)	
	Sump S4 8/18/81	Sump S5 8/18/81
Nicotine		Trace
Dichloroiodomethane		Trace
Bromodichloromethane	0.2	
Alkanes(C20-C31)	4	

a. No entry indicates compound is below detection level.

Note: The absence of many hydrophobic organic compounds, coupled with the low levels of hydrophilic species (Table 4) in water from experimental trench sections 4 and 5, suggests that there is little, if any, communication with waste trench 27.

TABLE 10. Comparison of Radionuclide Concentrations in Waste Trench Leachate (5-78) and Initial Experimental Trench Inflow (9-79)

	Concentration, pCi/l				
	³ H	Total Pu	⁹⁰ Sr	⁶⁰ Co	¹³⁷ Cs
Waste Trench 27 Leachate	5.9+08	4.8+03	2.1+05	1.3+03	8.0+03
Experimental Trench					
Section T1	3.7+08	3.6+01	6.7+03	3.6+01	6.5+01
Section T2E	1.7+09	6.1+01	1.7+05	2.2+02	1.6+03
Section T2W	4.2+09	3.4+03	1.6+05	9.7+03	4.6+03
Section T3E	3.4+09	5.0+03	1.1+05	6.0+03	9.0+01

Note: Radionuclide concentrations in water flowing into the experimental trench were comparable to concentrations in the waste trench 27 sump opposite section 2, indicating that subsurface migration of radionuclides had occurred in this limited region.

TABLE 11. Comparison of Radionuclide and Bromine Concentrations in Waste Trench Leachate (5-78 and 9-80) and Inert Atmosphere Wells (9-80)

	Radionuclide Concentration (pCi/l)				Bromine ppm
	³ H	²³⁸ Pu	^{239,240} Pu	⁹⁰ Sr	
Waste Trench 27 Sump (5-78)	5.9+08	4.1+03	6.7+02	2.1+05	2.8+00
Waste Trench 27 Sump (9-80)					4.6+02
Waste Trench 27 Well Point (9-80)					2.7+00
Well W1N	4.7+05	3.7+01	6.0+00	1.5+02	1.0+00
Well W2N	2.9+06	2.1+01	7.7+01	3.3+02	2.0+00
Well W2NA	7.7+08	2.4+02	4.8+00	1.7+04	1.2+02
Well W3N	1.2+09	2.4+03	4.4+01	3.4+04	8.2+02
Well W3NA	2.0+07	2.3+01	5.0+00	2.4+02	5.2+02
Well W5N	1.0+03	9.4+00	5.0+00	2.1+02	5.0+00

Note: Changes in bromine concentrations derived from the sodium bromide groundwater tracer added to the experimental trench indicate that communication exists between waste trench 27 and experimental area No. 1.

SECTION II

GEOCHEMISTRY OF TRENCH LEACHATES FROM MAXEY FLATS*

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SUMMARY

The characterization of trench leachates is necessary for identifying key geochemical controls on trench water chemistry and radionuclide mobility at the Maxey Flats disposal site. With this in mind, several trench leachates were sampled at Maxey Flats in October 1981.

Most trench waters from Maxey Flats exhibit low redox potential, low dissolved oxygen and sulfate, and high alkalinity, which are characteristic of anoxic waters. In contrast to naturally occurring anoxic waters, the Maxey Flats leachates also exhibit enrichments to varying degrees of waste-derived components such as dissolved iron, organic carbon, chloride, fluoride, sodium, strontium, barium, tritium and several other radionuclides.

The observed trench leachate chemistries reflect the extent of modification of infiltrated rainwater by a combination of processes, occurring simultaneously, such as bacterial degradation and leaching of buried waste. Given the variability and complexity of the trench water geochemical systems under investigation, it is not possible to quantitatively evaluate the magnitude of these processes without a knowledge of the characteristics and reactivity of the buried waste and the residence time of the leachates in the trenches. These are the key factors controlling the rate and extent of solute production in terms of radionuclides, cations and anions, and dissolved organics which, in turn, determine the extent of modification of infiltrated rainwater composition in a trench, resulting in the observed leachate chemistries.

Oxidation experiments performed on Maxey Flats and West Valley trench waters, spiked with Sr-85, Co-60, and Cs-137, provide generic information on the behavior of anoxic trench waters as they encounter a less reducing environment along the groundwater flow paths. The experiments demonstrated that, upon oxidation, a series of chemical changes were initiated which results in the oxidation of Fe^{2+} to ferric oxyhydroxide, a decrease in alkalinity, a slight increase in pH, and a drastic increase in Eh. The experiments further demonstrated that, even though precipitation of ferric oxyhydroxide occurred in most cases, coprecipitation or scavenging of Co-60, Sr-85, and Cs-137 was minimal. It appears that some of the radionuclides may have formed complexes with chelating agents sufficiently stable to withstand ferric oxyhydroxide scavenging. If such is the case, one can conclude that radionuclide mobility would not be substantially retarded by authigenic ferric oxyhydroxide, which occurs in geochemical systems where anoxic waters encounter an oxidizing environment.

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1. INTRODUCTION

Information on the chemical and radionuclide composition of trench leachates and on the processes that control radionuclide mobility is important in predicting radionuclide transport at shallow land burial sites. During the past several years, Brookhaven National Laboratory (BNL) has been involved in a field and laboratory program to study the source term characteristics of existing commercially operated low level radioactive waste disposal sites. As part of this overall effort, the Maxey Flats disposal site was sampled four times over a period of six years. Characteristics of trench waters collected during earlier sampling trips have been reported previously (Czyscinski and Weiss, 1981; Weiss and Colombo, 1980). In this report, we present the results of the analysis of trench leachates collected at Maxey Flats in October 1981 and a discussion of the factors controlling the trench water chemistry. In addition, results of oxidation experiments performed on both Maxey Flats and West Valley trench leachates, simulating the behavior of anoxic trench waters as they encounter upon migration an oxidizing environment, are presented. The experiments were conducted to determine the extent of radionuclide scavenging as a result of ferric oxyhydroxide precipitation.

In a separate topical report on Maxey Flats disposal site (in preparation), the trench water and sediment data generated to date at Brookhaven National Laboratory will be discussed. The available data will be interpreted using an integrated approach to identify key geochemical controls on trench water chemistry and the important factors controlling radionuclide migration in trench water-sediment systems.

2. EXPERIMENTAL

2.1 Field Sampling and Measurements

The location of the various trenches at the Maxey Flats disposal site is shown in Figure 2.1. Seven disposal trenches were sampled in October 1981 and one on-site well was sampled in May 1978 using anaerobic sampling procedures described earlier (Weiss and Colombo, 1980). In-line measurements of temperature, specific conductance, dissolved oxygen and sulfide, Eh and pH were performed using methods reported previously (Weiss and Colombo, 1980).

Figure 2.1 Map of the Maxey Flats disposal site, showing the location and identification of the disposal trenches. The exact location of the sump standpipes in the trenches is also shown as M in trench 23, W and S in trench 19S, 7-3 in trench 7, and 4 and 8 in trench 33L.

2.2. Laboratory Trench Water Analysis

The water samples were stored at 4°C and in an inert atmosphere to prevent oxidation. In the laboratory, an aliquot of each sample was filtered anaerobically through a 0.45 µm membrane filter and analyzed immediately for alkalinity (titration), ferrous and total iron (colorimetric), ammonia (probe), and pH (probe). Another fraction was filtered under similar, anaerobic conditions and the filtrate was analyzed for anions (chloride, fluoride, nitrate and sulfate by ion chromatographic analysis), dissolved inorganic carbon and total carbon (Beckman Carbon Analyzer). A third aliquot of each sample was filtered and acidified with ultrapure nitric acid and subsequently analyzed for radionuclides and dissolved metals.

Radionuclide analyses were performed by liquid scintillation counting (tritium), Ge-(Li) gamma-ray spectroscopy (Am-241, Co-60, Cs-134, Cs-137), and radiochemical separations (Sr-90, Pu-238, 239, 240). Atomic absorption methods were used to determine dissolved metals.

2.3 Oxidation Experiments

Leachate samples from several disposal trenches at Maxey Flats and West Valley were selected for the oxidation experiments. The West Valley trench leachates were included because, like most Maxey Flats trench waters, they also exhibit anoxic characteristics. The oxidation behavior of the trench leachates was studied in terms of pH, Eh, alkalinity, and radionuclide activities.

An aliquot of each sample was anaerobically transferred into an oxidation chamber in an argon filled glove box and spiked with Sr-85, Cs-137, and Co-60. The pH, Eh, and alkalinity were determined immediately upon transfer by standard analytical methods (Franson, 1981). Further, an aliquot of the initial sample was acidified with HCl and analyzed for initial concentrations of ferrous iron, total iron, Cs-137, Sr-85, and Co-60.

The oxidation chamber was removed from the glove box and the spiked trench water was exposed to air for approximately two weeks. Following complete air oxidation, the pH, Eh, and alkalinity were determined. The sample was filtered, acidified, and analyzed for Cs-137, Co-60, Sr-85, ferrous iron, and total iron.

Total dissolved iron was determined by atomic absorption. The sensitivity of the method is about 0.04 ppm Fe. The precision of the method, based on analysis of replicate samples, is better than 3 ppm at the total dissolved iron concentrations present in the trench leachates. Ferrous iron was determined colorimetrically by complex formation with 1,10-phenanthroline in an acidic solution. The precision of the method is better than 3 ppm at the Fe²⁺ concentrations in trench leachates. The detection limit of the method ranges from 1 to 4 ppm ferrous iron.

3. RESULTS AND DISCUSSION

3.1 Leachate Chemistry

Field measurements of pH, Eh, specific conductance, dissolved oxygen and sulfide, and temperature are compiled in Table 3.1. The major anion and cation compositions of the trench waters and well water UB1A are presented in Table 3.2.

Table 3.1

Field Measurements of Trench and Well Waters at Maxey Flats Disposal Site

Trench	Temperature (°C)	Specific Conductance (µmho/cm)	Dissolved Oxygen (mg/L)	Eh (mV, SHE ^a)	pH	Sulfide ^b (mV)
7-3	16.5	12000	0.10	-44	7.4	-324
19W	15.0	2100	0.10	-27	6.5	-465
23M	17.0	4800	0.05	-38	7.5	-302
27	16.0	6600	<0.05	+17	6.8	-353
33L4	17.0	6400	0.05	-54	12.0	-278
33L8	18.0	2000	0.25	-135	6.0	-125
35	17.0	3400	0.10	-14	8.2	-486
Well Water UB1A	12.4	2310	0.20	+274	6.6	c

^aStandard hydrogen electrode.

^bThe sulfide electrode was calibrated in the laboratory using the method developed by Berner (1963).

^cNot determined.

Table 3.2

Composition of Trench Waters and Well Water From Maxey Flats Disposal Site

	Concentrations (mg/L)							Well Water UB1A
	Trench Water							
	7-3	19W	23M	27	33L4	33L8	35	
<u>Anion</u>								
Chloride	2500	231	575	2340	361	37	235	350
Fluoride	44	4.0	5.3	<0.1	<0.1	3.7	45	a
Nitrate (as N)	8.5	0.5	28	17	9.9	1.6	0.7	<0.1
Sulfate	1320	<1.5	5.8	<1.5	<1.5	15	<1.5	1700
<u>Cation</u>								
Ammonium (as N)	75	45	100	116	26	50	37	350
Barium	<0.5	0.7	<0.5	14.5	7.3	<0.5	0.5	<2
Calcium	107	49	11	220	864	190	26	180
Iron-total	16	65	7	165	0.2	43	0.9	<0.1
Iron-Ferrous	12	62	6	164	a	42	0.8	<0.5
Magnesium	193	128	230	350	<0.2	49	330	300
Manganese	2	0.5	<0.1	1.7	<0.1	1.9	0.3	<0.1
Potassium	329	27	77	87	102	11	51	12
Sodium	2140	231	825	554	180	50	614	530
Strontium	0.7	0.6	~0.3	2.3	8.0	~0.3	~0.3	2.6
<u>Other Constituents</u>								
pH	7.6	6.8	7.7	6.6	12.0	6.4	8.4	a
Total Alkalinity (as CaCO ₃)	1150	1040	2420	312	2120	1080	2310	30
Hardness (Mg+Ca) (as CaCO ₃)	1060	650	975	1990	2160	675	1430	1700
Inorganic Carbon	220	170	520	57	1	330	390	15
Organic Carbon ^b	730	430	780	493	1500	160	540	5
^a Not determined.								
^b Dissolved organic carbon is calculated from the difference between total and inorganic carbon.								

^aNot determined.^bDissolved organic carbon is calculated from the difference between total and inorganic carbon.

3.1.1 Ion Balance of Major Anions and Cations

An ion balance of the major cations and anions present in each leachate sample was conducted to determine the completeness of the trench water analyses. Equivalents of the major cations and anions were compared as shown in Figure 3.1. The percent ion balance error (e) was estimated using the following equation:

$$e = \frac{\sum_c - \sum_a}{\sum_c + \sum_a} \cdot 100 \quad (3.1)$$

where $\sum_c$ and $\sum_a$ represent the cation and anion sums (meq/L), respectively. Table 3.3 shows that the maximum ion balance error is less than 5%, suggesting that the analyses are relatively complete and accurate. An error in the analysis or an element which might have not been determined do not appear to be significant to the extent that they would affect the major ion composition of the trench waters.

Figure 3.1 Ion balance for major cations and anions in Maxey Flats trench waters.

Table 3.3

Ion Balance of Major Anions and Cations for Maxey Flats Trench Waters

Disposal Trench	Ion Concentration (meq/L)		Ion Balance Error (%)
	Anion Sum	Cation Sum	
7-3	124	129	1.9
19W	27.6	29.2	2.8
23M	68.1	64.7	-2.6
27	73.5	80.6	4.6
33L4	53.4	55.7	2.1
33L8	23.3	21.1	-4.9
35	55.3	59.2	3.4

3.1.2 Trench Water Composition

Field measurements for the Maxey Flats trench leachates show that for all the trenches sampled the dissolved oxygen levels are either very low or below the detection limit, indicating anoxic conditions in the trenches. Anoxic conditions are also indicated by the negative redox (Eh) and sulfide potentials. The sulfide potentials reported in Table 3.1 lie outside the calibration range, indicating very low concentrations of dissolved sulfide in the trenches ($<10^{-12}$ M). The pH values measured in the trench leachates range from 6.0 to 8.2, except for 33L4 which has a pH of 12.0. This anomalously high pH can be attributed to the leaching of cement, which was used as a matrix for in-trench solidification of liquid waste. The relatively high specific conductance observed for leachate 7-3 can be attributed to the very high concentrations of Cl^- and Na^+ ions present in the trench water.

The cation and anion equivalents in the Maxey Flats leachates are plotted on trilinear diagrams in Figures 3.2 and 3.3. For comparison purposes, data from well UB1A is also displayed on the ternary plots.

Figure 3.2 indicates that relative to all trench waters examined, leachate 33L4 shows significant enrichment in Ca^{2+} . As evident from data presented in Table 3.2, enrichments of Sr^{2+} and Ba^{2+} are also observed in trench leachate 33L4. The highest concentration of Ba^{2+} is observed in trench 27, with a value approaching 14.5 mg/L. Trench water 7-3 exhibits an extremely high concentration of Na^+ , relative to other leachates and well water UB1A. Table 3.2 indicates further that most of the total dissolved iron present in the trench leachates occurs in the ferrous state and that the total dissolved iron concentrations are high compared to well water UB1A.

Figure 3.2 Trilinear diagram displaying major cation compositions of Maxey Flats trench waters and well water UB1A.

The anion compositions illustrated in Figure 3.3 show that all trench waters, except leachate 7-3, are depleted in SO_4^{2-} relative to well water UB1A, which contains approximately 80% of the total anion equivalents of the water. In trenches 19W, 27, 33L4, and 35, the sulfate concentrations were below the detection limit of 1.5 mg/L. This indicates that sulfate reduction may be taking place in the trenches. The reduction of sulfate is supported by the observations of low redox potentials, low dissolved oxygen concentrations, and high alkalinities in the trench waters. In addition, sulfate reducing bacteria have been detected in the Maxey Flats trench waters (Francis et al., 1980).

Relative to the very low concentration of NO_3^- in well water UB1A (Table 3.2), the NO_3^- concentrations in the trench leachates are significantly higher, indicating a waste-derived source. Similarly, leaching of buried waste most likely contributes to the high concentrations of Cl^- in trenches 7-3 and 27 and F^- in trenches 7-3 and 35.

Figure 3.3 Trilinear diagram displaying major anion compositions of Maxey Flats trench waters and well water UB1A.

Comparison of dissolved carbon concentrations in trench leachates with that in well water UB1A indicates significant enrichment of both organic and inorganic carbon in the trench waters. The carbon enrichments in the leachates can be attributed to the leaching or decomposition of wastes in the trenches.

3.1.3 Dissolved Radionuclides in Trench Leachates

The activities of H-3, Am-241, Co-60, Cs-134, Cs-137, Pu-238, Pu-239, 240, and Sr-90 in the trench leachates are presented in Table 3.4. These data show that tritium is the most abundant radionuclide with the highest concentration approaching 5.5×10^9 pCi/L in trench leachate 35. This is more than an order of magnitude lower than 10^{11} pCi/L, previously reported for trench 31 which is believed to contain approximately two-thirds of the entire tritium inventory (currently ~300,000 Ci) at Maxey Flats (E. O'Donnell, personal communication).

Table 3.4

Concentration of Dissolved Radionuclides in Maxey Flats Trench Waters

Radionuclide	Activity pCi/L (+2σ) ^a						
	Trench 7-3	Trench 19W	Trench 23M	Trench 27	Trench 33L4	Trench 33L8	Trench 35
H-3	3.0x10 ⁸ (3)	9.8x10 ⁷ (6)	1.3x10 ⁹ (3)	1.9x10 ⁹ (3)	4.4x10 ⁷ (3)	1.3x10 ⁷ (3)	5.5x10 ⁹ (1)
Am-241	3.9x10 ² (25)	4.5x10 ⁴ (1)	1.4x10 ² (20)	3.0x10 ² (20)	<40	<30	4.4x10 ² (8)
Co-60	1.6x10 ³ (3)	2.9x10 ⁴ (1)	1.5x10 ³ (2)	5.8x10 ³ (1)	1.4x10 ¹ (10)	1.4x10 ² (8)	1.5x10 ² (9)
Cs-134	1.0x10 ² (40)	<50	<20	4.5x10 ¹ (30)	<20	<20	1.8x10 ² (9)
Cs-137	1.0x10 ⁵ (1)	1.2x10 ⁴ (1)	3.2x10 ³ (1)	1.2x10 ⁴ (1)	<60	8.9x10 ¹ (10)	1.0x10 ⁴ (1)
Pu-238	9.3 (16)	3.5x10 ⁵ (5)	2.2x10 ⁴ (5)	8.9x10 ³ (6)	4.3x10 ² (5)	7.9 (18)	5.1x10 ³ (5)
Pu-239,240	2.6 (36)	9.6x10 ² (5)	6.9x10 ¹ (7)	1.8x10 ² (9)	8.4x10 ³ (5)	1.2 (50)	7.1x10 ¹ (5)
Sr-90	3.2x10 ⁵ (0.11)	2.4x10 ⁵ (0.10)	1.9x10 ⁴ (0.42)	2.9x10 ⁴ (0.97)	1.5x10 ⁴ (0.44)	4.4x10 ² (1.4)	1.5x10 ⁴ (0.45)

^aThe number in () represents 2σ counting uncertainty.

An inter-trench comparison of the observed radionuclides shows that, following tritium, Sr-90 is the most dominant radionuclide in practically all the trench leachates sampled. The highest concentrations of Sr-90, on the order of 3×10^5 pCi/L, are observed in trench leachates 19W and 7-3. The highest total radionuclide activities are present in trench waters 19W and 7-3. In contrast, leachate 33L4 exhibited the lowest total activity. Relatively high activities of Pu-238 are observed in trench waters 19W, 23M, 27, and 35. Trench leachates 19W and 27 were also analyzed for ^{237}Np . In both cases, the concentrations were below the detection limit of 10 pCi/L.

3.1.4 Geochemical Controls on Trench Water Chemistry

Most Maxey Flats trench waters are characterized by low redox potential, low sulfate and dissolved oxygen concentrations, high titration alkalinities, and the presence of ammonia. In comparison to naturally occurring, chemically reducing anoxic waters, Maxey Flats trench leachates also contain highly variable contents of waste-derived components such as dissolved iron, Cl^- , NO_3^- , dissolved carbon, tritium and several other radionuclides.

The development of anoxic conditions in trench water can be attributed to bacterial degradation of organic material in the waste. During the decomposition process, dissolved oxygen in the trench leachate is consumed. Since the waste trenches are located in relatively impermeable shale, the infiltrating rainwater tends to accumulate, whereby stagnant conditions prevail in the trenches. As a result of such static, closed system conditions, the accumulated waters have a long residence time in the trenches. Given these conditions in the trenches, the aerobic and anaerobic decomposition processes proceed in the sequence given below:

DEVELOPMENT OF ANOXIC CONDITIONS IN TRENCH WATER (BACTERIAL DEGRADATION OF ORGANIC MATTER)

OXYGEN CONSUMPTION

<u>CONSUMED</u>	<u>PRODUCED</u>
O_2	$\text{CO}_2, \text{NH}_4^+$

DENITRIFICATION

<u>CONSUMED</u>	<u>PRODUCED</u>
NO_3^-	CO_2, N_2

SULFATE REDUCTION

<u>CONSUMED</u>	<u>PRODUCED</u>
SO_4^{2-}	$\text{CO}_2, \text{NH}_4^+, \text{HS}^-$

The trench leachate composition reflects the extent of modification of infiltrated rainwater by a combination of processes such as bacterial degradation and leaching of waste. The rate and extent of these processes are primarily determined by the nature and quantity of the organic matter in the waste, the residence time of the accumulated trench water, and the rate of solute production in terms of radionuclides, cations, and anions as controlled by the reactivity of the waste.

During bacterial degradation of organic matter, there is a buildup of decomposition products such as ammonia and PCO_2 which causes alkalinity to increase. The extent of this buildup is a direct function of the quantity or quality of organic material present in the waste and of the ambient environmental conditions. In addition, dissolved oxygen, sulfate, and nitrate are consumed during aerobic and anaerobic oxidation of organic matter, resulting in low Eh values. Iron reduction contributes to high concentrations of dissolved iron, present primarily as Fe^{2+} . Undetectably low sulfate concentrations in trenches 19W, 27, 33L4, and 35 indicate that sulfate reduction is taking place. However, the observation of low sulfide concentrations in the trench leachates may reflect its removal by precipitation as iron sulfides, with the residual dissolved iron in the leachates representing iron in excess of the amount required by S^{2-} for precipitation.

Because of the low permeability of shale in the study area, the accumulated water has a relatively long residence time in the trenches. This allows prolonged leaching of the buried waste, resulting in elevated concentrations of waste-derived components such as Fe^{2+} , dissolved organic carbon, Cl^- , and several radionuclides. For example, the relatively high concentrations of Ca^{2+} and CO_3^{2-} in trench leachate 33L4 can be attributed to their release from the leaching of concrete, which is used as a solidification agent for immobilizing liquid waste disposed of in this trench. An extremely high pH value of 12, reported for trench leachate 33L4, further reflects the influence of the concrete matrix on the leachate chemistry.

Among the trench leachates sampled, Table 3.4 indicates that trench 33L4 exhibited the lowest concentrations of Cs-137, Co-60, and Am-241, as well as the lowest total activity (excluding that of tritium). This observation can be attributed to the solidification of liquid waste in trench 33L4. In contrast, most of the other trenches received uncompacted, readily leachable solid waste, thus resulting in higher concentrations of dissolved radionuclides in the trenches.

The high concentrations of chloride in trenches 7-3 and 27, fluoride in trenches 7-3 and 45, sodium in 7-3, and barium in 27 are probably generated from the leaching of waste. Similarly, elevated concentrations of both organic and inorganic dissolved carbon and dissolved iron in the leachates also indicate a waste-derived source.

The relatively high concentrations of NO_3^- and NH_4^+ in some of the leachates indicate that both nitrogen species are derived from the leaching of waste. The sources of ammonia in the buried waste could be ammonium sulfate found in decontaminating solutions and sodium ammonium sulfate from chemical regeneration of ion-exchange beds. A part of the NH_4^+ present could have formed during the processes of nitrate reduction, iron reduction, and sulfate reduction. However, the anomalous presence of high levels of NO_3^- in leachates 27 and 33L4, where depletion of both sulfate and dissolved oxygen is observed, is difficult to explain.

Although the observed leachate chemistries are a result of a combination of processes occurring in the trenches, it is not possible to quantitatively evaluate the magnitude of these processes without a knowledge of the characteristics and reactivity of the buried waste and the residence time of the leachate in the trenches. These are the important factors controlling the rate and extent of solute production in terms of radionuclides and other dissolved constituents, which determine the extent of modification of accumulated rainwater composition in a trench, resulting in the observed leachate chemistries.

3.2 Oxidation Behavior of Trench Leachates

The changes observed in pH, Eh, alkalinities, and radionuclide concentrations, upon air oxidation of radionuclide-spiked Maxey Flats and West Valley trench leachates, are presented in Table 3.5. The changes in the concentrations of Fe^{2+} and total dissolved iron are given in Table 3.6. Also listed in Table 3.6 are the acid generating potentials of the leachates, based on the ferrous to ferric oxidation reaction.

The results in Table 3.5 indicate that all trench waters, upon air oxidation, exhibit removal of most of the iron from solution, as a result of ferric oxyhydroxide precipitation. A reddish-brown precipitate was observed in all experiments, except 33L4.

Table 3.5

Observed Changes in pH, Eh, Alkalinity, and Radionuclide Concentrations
Upon Air Oxidation of Maxey Flats and West Valley Trench Leachates

Trench Water	Sampling Date	pH ^a		Eh(mV) ^a		Alkalinity (meq/L) ^a		Radionuclide in Solution After Oxidation (%)		
		Initial	Oxidized	Initial	Oxidized	Initial	Oxidized	Sr-85	Cs-137	Co-60
<u>Maxey Flats</u>										
7-3	10/81	7.5	8.1	-43	+402	25	19	86	104	97
19S	10/79	7.1	8.2	-58	+399	21	18	86	101	98
19W	10/81	6.7	7.7	-26	+411	22	19	92	100	92
23M	10/81	7.7	8.7	-95	+394	51	47	97	104	93
26	10/79	6.5	8.3	-52	+413	19	19	92	94	90
30	10/79	7.9	8.4	-37	+398	135	99	99	98	99
33L4	10/81	11.3	10.8	+150	+246	34	23	88	104	99
33L8	10/81	6.2	8.2	+79	+379	24	10	33	101	37
35	10/81	8.2	8.4	-83	+399	47	47	94	101	91
<u>West Valley</u>										
4	10/78	6.9	7.9	-10	+416	20	13	102	103	93
5	10/78	6.9	6.8	-50	+261	52	51	102	103	87
9	10/78	6.9	7.9	+12	+390	31	31	90	96	93

^aThe initial measurements were made immediately following sample transfer in the glove box.

Table 3.6

Changes in Ferrous Iron and Total Dissolved Iron Concentrations
Upon Air Oxidation of Maxey Flats and West Valley Trench Leachates
([H⁺] represents the acid generating potential of the leachate)

Trench Water	Dissolved Iron Concentration (mg/L)				[H ⁺] (meq/L) ^a
	Initial		Oxidized		
	Fe ²⁺	Fe _T	Fe ²⁺	Fe _T	
<hr/>					
<u>Maxey Flats</u>					
7-3	15	15	<1	0.4	0.54
19S ^b	53	49	<4	0.8	1.9
19W ^b	68	71	<4	8	2.4
23M ^b	6	3	<1	0.3	0.2
26	90	100	<4	1.1	3.2
30 ^b	3	1.5	2	0.8	0.1
33L4	<1	1.1	<1	0.18	<0.04
33L8	23	45	<1	0.5	0.82
35 ^b	2	1.5	<1	0.2	0.08
<hr/>					
<u>West Valley</u>					
4	91	154	<4	0.1	5.5
5	91	272	<4	1.0	9.7
9	25	28	<4	0.3	1.0

^aAcid generating potential calculated based on oxidation of dissolved ferrous iron according to Eqs. (1) and (2).

^bThe differences in the ferrous iron and total iron concentrations are not significant, considering the analytical precision of the two methods.

3.2.1 Eh, pH and Alkalinity

For the majority of trench waters, oxidation resulted in an increase in pH. A slight decrease in pH was observed for the Maxey Flats trench water 33L4. This leachate is atypical of most Maxey Flats trenches, however, in that the disposed waste was solidified in a concrete matrix. Another notable exception, Maxey Flats leachate 27 containing high Fe²⁺ concentration and low alkalinity, was discussed in a previous report (Pietrzak et al., 1983). Air oxidation of this leachate resulted in a drastic drop in pH. The pH changes can be attributed to a combination of three principal processes occurring simultaneously during oxidation: (a) loss of CO₂ as a result of exposure of the trench water to the lower partial pressure of CO₂ in air; (b)

generation of acidity during oxidation of ferrous to ferric iron; and (c) neutralization of resulting acidity by trench water alkalinity. As discussed earlier, during the development of an anoxic water regime, bacterial degradation processes liberate carbon dioxide which raises the P_{CO_2} of the anoxic water. Upon exposure to air, the pH of naturally occurring anoxic waters normally rises, as a result of CO_2 loss and subsequent readjustment of the chemical system (Pietrzak et al., 1982).

The principal mechanism which would decrease the pH is the oxidation of dissolved ferrous iron. Ferrous to ferric iron oxidation may be represented as:

Each equivalent of ferrous iron that is oxidized and precipitated as ferric hydroxide produces two equivalents of hydrogen ion. Since all the dissolved iron is in the ferrous state in most trench leachates being studied (Table 3.6) and available for oxidation, calculations show the acid generating potential in meq/L of H^+ which could be generated from the Fe^{2+} oxidation reaction (Table 3.6). However, the resulting acidity can be neutralized by the trench water alkalinity. The meq/L of buffering capacity of each trench leachate available from the titration alkalinity is given in Table 3.5.

The changes in pH of trench water resulting from oxidation are interpreted in terms of these competing reactions. For waters with high ferrous iron and alkalinity such as Maxey Flats leachates 19S, 19W, 26 and West Valley leachates 4 and 5, the available buffering capacity is well in excess of that required to neutralize the acidity created during iron oxidation. The exception is Maxey Flats leachate 27, where the acidity generated as a result of the oxidation of high concentration of ferrous iron in solution is well in excess of the buffering capacity. Consequently, as discussed in earlier reports (Pietrzak et al., 1982; Pietrzak et al., 1983), a sharp drop in pH is observed upon oxidation of leachate 27 which, in turn, inhibits complete oxidation of ferrous iron to ferric hydroxide. For Maxey Flats leachates containing relatively low concentrations of Fe^{2+} iron such as trenches 23M, 30, and 35 but with high alkalinity, exposure to air results in a release of excess P_{CO_2} , developed during bacterial degradation, and a subsequent rise in pH. Similar behavior has been reported in naturally occurring anoxic waters.

An Eh-pH plot, showing the principal stability fields in the Fe-O-H₂O-CO₂-S system, is displayed in Figure 3.4. The trench water data, as represented by open circles and triangles for Maxey Flats and West Valley sites, are plotted in Figure 3.4 to illustrate the positions of these data points relative to the stability fields of the principal solute species and mineral phases. All data points, except for 33L4, lie in the ferrous iron

mineral stability regions, reflecting the anoxic character of these waters. This is also supported by the low redox potential and dissolved oxygen contents of the trench waters. Although trench water 33L4 exhibits similar redox potential as the trench waters in equilibrium with ferrous mineral phases, the data point lies in the ferric hydroxide stability region because its $[H^+]$ concentration is four orders of magnitude lower. As mentioned before, this elevated pH is a result of the leaching of concrete, which was used as a matrix for solidifying the liquid waste.

The data points representing oxidized trench waters (denoted by solid circles and triangles) lie in the ferric hydroxide stability field as well as the data point UB1A, representing well water.

Figure 3.4 Eh-pH relationship for oxidized and reduced water samples collected from Haney Plant and West Valley sites. Data were collected after the 1973 earthquake (10-20) and 1974 (20-30) and 1975 (30-40) and 1976 (40-50) and 1977 (50-60) and 1978 (60-70) and 1979 (70-80) and 1980 (80-90) and 1981 (90-100).

Figure 3.4 Eh-pH relationships for initial and oxidized water samples collected from Maxey Flats and West Valley sites. Diagram modified after Hem (1972). Dissolved $\Sigma\text{CO}_2 = 10^{-3}\text{M}$; $\Sigma\text{SO}_4^{2-} = 10^{-4}\text{M}$; and $\Sigma\text{Fe} = 10^{-3}\text{M}$ to 10^{-7}M .

3.2.2 Dissolved Radionuclides

Based on the data in Table 3.6, it is clear that almost all trench waters upon oxidation exhibit removal of dissolved iron from solution, as a result of ferric oxyhydroxide precipitation. However, the radionuclide data in Table 3.5 indicates that coprecipitation or scavenging of Co-60, Cs-137, and Sr-85 by the resultant precipitate is minimal. Among the radionuclides studied, Cs-137 is removed the least from solution, followed by Co-60 and Sr-85. The maximum removal of Sr-85 is observed in leachate 33L8 with values approaching 67% and 63% of the initial amounts present. The lack of substantial removal of dissolved radionuclides in most oxidized trench waters, even in the presence of a ferric oxyhydroxide precipitate, may suggest complexation of radionuclides with chelating agents, especially considering that relatively large concentrations of dissolved organic carbon are also present. Low concentrations of some organic chelating agents such as NTA, DTPA, and EDTA have been reported in these trench waters (Weiss et al., 1982). Recently, Kirby et al. (1983) reported total dissolved EDTA concentrations of 1 to 4 ppm in trench 27 and 19S leachates. In an earlier report (Pietrzak et al., 1983), we presented data on the oxidation behavior of West Valley leachate 8 as a function of time, showing that, even though ferric oxyhydroxide precipitation occurred upon air oxidation of the leachate, coprecipitation of dissolved radionuclides was minimal. Cleveland and Rees (1981) made a similar observation for dissolved Pu in Maxey Flats trench leachates, where plutonium is reported to exist primarily as complexes of the tetravalent ion with strong organic ligands such as EDTA. Only partial precipitation of dissolved plutonium by ferric hydroxide was reported. Work at Pacific Northwest Laboratories also provides circumstantial evidence for radionuclide complexation in trench leachates at Maxey Flats. Kirby and Toste (1982) reported generally good correlation between Pu and Co-60 and EDTA, and between Sr-90 and Cs-137 and carboxylic acids in leachate samples from experimental wells located 4-7 m from trench 27.

Further experiments are planned to determine the role of organic chelating agents in preventing radionuclide scavenging by ferric oxyhydroxide precipitation.

4. CONCLUSIONS

Most trench waters from Maxey Flats exhibit low redox potential, low dissolved oxygen and sulfate, and high alkalinity, which are characteristic of anoxic conditions. In contrast to naturally occurring anoxic waters, the Maxey Flats leachates also exhibit enrichments to varying degrees of waste-derived components such as dissolved iron, organic and inorganic carbon, chloride, fluoride, sodium, strontium, barium, tritium and several other radionuclides.

The observed trench leachate chemistries reflect the extent of modification of infiltrated rainwater by a combination of processes, occurring simultaneously, such as biodegradation and leaching of buried waste. Given the variability and complexity of the trench water geochemical systems under

investigation, it is not possible to quantitatively evaluate the magnitude of these processes without a knowledge of the characteristics and reactivity of the buried waste and the residence time of the leachate in the trenches. These are the key factors controlling the rate and extent of solute production in terms of radionuclides and other dissolved constituents which, in turn, determine the extent of modification of accumulated rainwater composition in a trench, resulting in the observed leachate chemistries.

Air oxidation of anoxic Maxey Flats and West Valley trench waters demonstrated that, even though precipitation of ferric hydroxide occurred in most cases, coprecipitation or scavenging of Co-60, Sr-85, and Cs-137 was minimal. Considering that high concentrations of dissolved organic carbon are present in the leachates and that some organic chelating agents such as NTA, DTPA, and EDTA have also been reported, we believe that some of the radionuclides may have formed complexes sufficiently stable to withstand ferric oxyhydroxide scavenging. If such is the case, one can conclude that radionuclide mobility would not be substantially retarded by authigenic ferric oxyhydroxide, which occurs in geochemical systems where anoxic waters encounter an oxidizing environment.

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SECTION III

INFLUENCE OF SOIL CHEMISTRY ON THE
MOBILITY OF PuEDTA

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INFLUENCE OF SOIL CHEMISTRY ON THE MOBILITY OF PuEDTA

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ABSTRACT

More than 95% of the soluble Pu in a low-level radioactive waste burial trench at the Maxey Flats, Kentucky shallow land-burial site is complexed with ethylenediaminetetraacetic acid (EDTA) as mobile PuEDTA species. *In situ* chemical measurements and thermodynamic considerations are used to explain the reduction in Pu concentration as the waste moves a few meters from the trench through the soil. Relative to total EDTA, the concentrations of PuEDTA and EDTA^{4-} are less in the soil solutions than in the trench waste; the inorganic Fe concentration is greater. Those observations suggest that the concentration of FeEDTA increases because of the increase in inorganic Fe, thus reducing the EDTA^{4-} concentration. As a result, PuEDTA dissociates to maintain its equilibrium with EDTA^{4-} . Additional sorption takes place because of an increase in inorganic Pu, which causes the Pu complex to dissociate even more.

I. INTRODUCTION

The Maxey Flats low-level waste burial site is one of the six original sites licensed for shallow land-burial of low level radioactive commercial waste in the United States. The Maxey Flats site is located in northcentral Kentucky about 24 km northwest of the town of Morehead. It is situated on a flat mesa about 150 m above the surrounding valleys. The site was opened in May 1963 and had accumulated about 40% of all the commercially generated low-level radioactive waste buried in the United States by the time it was closed in December 1977. A problem of serious concern at the time of closure was the excessive entry of water into the burial trenches and the subsequent movement of the liquid waste and its associated radionuclides from the trenches into the surrounding soil environment. The plutonium associated with the liquid waste in the burial trenches is complexed with ethylenediaminetetraacetic acid (EDTA), a highly stable commercial chelating agent,^{1,2} and thus is believed to be highly mobile.

An evaluation of the distribution of waste and its associated radionuclides in soil near a burial trench (Trench 19S) indicates that waste has moved out to a distance of 6 to 10 m from the trench; tritium in the waste liquid was used as a tracer of the movement of waste liquid. Plutonium also moved out into the soil but to a much lesser extent than did tritium. The difference in movement of those two radionuclides was attributed to the influence of soil chemistry on the mobility of PuEDTA through soil.³

The purpose of this study is to evaluate the feasibility of thermodynamic modeling of PuEDTA mobility (stability) under laboratory and field conditions and to evaluate the influence of soil chemistry on the mobility of PuEDTA.

II. MATERIALS AND METHODS

A. Laboratory Experiments

Laboratory experiments were conducted using liquid waste from Trench 19S of the Maxey Flats site and using the Ap and C horizon soils of the Tilsit series, the predominant soil series at the Maxey Flats burial site. In one experiment, Trench 19S waste was collected under anoxic conditions, spiked with ^{238}Pu and $^{239,240}\text{Pu}$ and aliquots allowed to equilibrate under ambient laboratory conditions for periods of approximately 1 hr, 5 days, and 6 days. At the end of the equilibration periods, the waste aliquots were centrifuged to remove particulates greater than $0.05\ \mu\text{m}$ nominal diameter. Analytical measurements were performed on the centrifuged solution to define the characteristics of the soluble fraction (less than $0.05\ \mu\text{m}$ diameter) of the waste. Those measurements included pH, electrical conductivity (EC), Eh, plutonium, iron, calcium, magnesium, and dissolved organic carbon (DOC). The charge characteristics of plutonium, iron, calcium, and magnesium were determined using cation-, anion-, and mixed-bed-exchange resins. Those data are given in Table I.

The total concentration of plutonium was 2.1×10^{-6} moles/L; the soluble concentration was several orders of magnitude less than that. The difference between those two concentrations can be attributed to the presence of a $\text{Pu}(\text{OH})_4$ precipitate. Visual observation of the equilibrated waste aliquots also indicated the presence of precipitated iron, probably ferrosic hydroxide $[\text{Fe}_3(\text{OH})_8]$.⁴ Thermodynamic considerations were used to calculate an ion activity product (IAP) for $\text{Pu}(\text{OH})_4$. That IAP was then compared with the solubility product (K_{sp}) found in the literature.⁵

TABLE I

CHEMICAL AND PHYSICAL MEASUREMENTS OF SPIKED MAXEY FLATS TRENCH 19S WASTE EQUILIBRATED UNDER OXIC LABORATORY CONDITIONS

	Waste 1	Waste 2	Waste 3
pH	7.54	7.67	7.88
Eh (v)	0.39	0.45	0.43
EC (dS/m)	2.16	2.04	1.99
Total Alkalinity as CaCO_3 (ppm)	870	863	860
DOC (ppm)	400	400	440
Ca (ppm)	32	36	30
Mg (ppm)	122	140	110
Fe (moles/L)	1.7×10^{-5}	1.7×10^{-5}	2.0×10^{-5}
% Cationic	18	31	17
% Anionic	65	51	69
% Neutral	17	18	14
Pu (mole/L)	3.5×10^{-9}	1.6×10^{-8}	2.2×10^{-8}
% Cationic	2 ± 1	4 ± 2	2.3 ± 0.1
% Anionic	93 ± 4	82 ± 5	92 ± 4
% Neutral	5 ± 4	14 ± 7	6 ± 4

In another experiment, at the time that the plutonium spike was added to the Trench 19S waste, aliquots of that waste were added to Ap and C horizon soils. Those waste/soil systems were equilibrated for 5 days and 6 days, respectively. As in the case of the waste system, the waste/soil systems were centrifuged and analyses performed on the centrifuged solution. The analyses were the same as those performed on the waste system. Those results are given in Table II. Thermodynamic considerations were used to evaluate the concentration of inorganic species of reduced plutonium [Pu(III,IV)]. Distribution coefficients (K_d) were then determined for inorganic Pu(III,IV). Those coefficients were compared with K_d evaluated elsewhere.⁶

B. Field Experiment

Onsite measurements were performed on Trench 19S waste and soil solutions collected from porous cup samplers located in vertical and horizontal arrays near Trench 19S at the Maxey Flats burial site. Onsite measurements included pH, Eh, alkalinity, and EC. Also, aliquots of samples were passed through cation-, anion-, and mixed-bed ion-exchange resins. Further analyses were performed in the laboratory and include those of plutonium, iron, calcium, magnesium, and DOC. Some of the same analyses were performed on the aliquots passed through ion-exchange resins and on the resins after digestion. The data are presented in Table III. Thermodynamic considerations were used to calculate the inorganic species of Pu(III,IV). Plutonium analyses of soil in which the porous cup samplers were located were also performed. Distribution coefficients of inorganic Pu(III,IV) were calculated and compared with those determined in the laboratory experiment.

TABLE II
SELECTED CHEMICAL AND PHYSICAL CHARACTERISTICS OF SPIKED
MAXEY FLATS TRENCH 19S WASTE-TILSIT SOIL SYSTEMS

	Tilsit Ap Soil	Tilsit C Soil
pH	6.71 ± 0.02	6.11 ± 0.02
Eh (mV)	492 ± 5	490 ± 16
EC (dS/m)	1.51 ± 0.01	0.86 ± 0.01
Total Alkalinity as CaCO ₃ (ppm)	378 ± 1	86 ± 7
DOC (ppm)	475 ± 9	400 ± 10
Ca (ppm)	33 ± 1	1.3 ± 0.3
Mg (ppm)	110 ± 20	7 ± 1
Fe (moles/L)	(1.1 ± 0.4) × 10 ⁻⁵	(4.8 ± 0.3) × 10 ⁻⁶
% Cationic	37 ± 9	47 ± 8
% Anionic	43 ± 10	35 ± 7
% Neutral	20 ± 3	19 ± 2
Pu (moles/L)	(2.1 ± 0.4) × 10 ⁻⁹	(3.1 ± 1.5) × 10 ⁻¹⁰
% Cationic	3 ± 2	31 ± 11
% Anionic	71 ± 18	58 ± 24
% Neutral	28 ± 17	12 ± 7

TABLE III

**IN SITU CHEMICAL AND PHYSICAL CHARACTERISTICS OF
TRENCH WASTE AND SOIL SOLUTIONS FROM THE TRENCH 19S
STUDY AREA OF THE MAXEY FLATS BURIAL FACILITY**

	Trench Waste	Soil Solutions		
		Approximate Distance from Trench (m)		
		1.5	3.0	6.0
^3H (pCi/L)	7.8×10^7	2.3×10^7	7.3×10^6	2.0×10^4
Waste Dilution Factor	—	3.0	10.8	4.1×10^3
pH	7.25	6.80	6.30	5.60
Eh (mV)	-78	72	330	240
EC (dS/m)	1.55	1.41	3.1	3.3
DOC (ppm)	106	57	15	18
Alkalinity as CaCO_3 (ppm)	585	575	278	78
Fe (moles/L)	6.45×10^{-4}	2.54×10^{-4}	2.33×10^{-6}	5.39×10^{-3}
% Cationic	67	68	22	81
% Anionic	29	28	26	7
% Neutral	4	4	52	12
Pu (mole/L)	1.53×10^{-11}	4.75×10^{-13}	$<6.14 \times 10^{-14}$ $\geq 7.6 \times 10^{-16}$	$<6.4 \times 10^{-14}$ $\geq 2.2 \times 10^{-15}$
% Cationic	10	2	70	0
% Anionic	89	97	30	100
% Neutral	1	1	0	0

C. Thermodynamic Considerations

Thermodynamic or equilibrium relations are used in this study to determine species concentrations that cannot be readily determined analytically but are needed in the evaluation of the behavior of plutonium. For example, soil and sediments adsorb the reduced inorganic species of plutonium to a much greater extent than the oxidized inorganic species of plutonium.⁶ Therefore, distribution coefficients based on the concentration of reduced species in solution should provide more meaningful information in interpreting the mobility of plutonium even though that concentration is much less than the oxidized species or the reduced organic species of plutonium. In those cases, thermodynamic relations were used to determine their concentrations. Also, the concentrations of the PuEDTA species in solution are controlled by the relative concentrations of inorganic plutonium species and by the concentration of noncomplexed EDTA ligand. The thermodynamic approach provides a means of evaluating those relative concentrations.

The basic assumptions used in the thermodynamic considerations include the following.

1. The two metal constituents of importance in controlling the concentration of PuEDTA are plutonium and iron. Iron competes with plutonium for the EDTA ligand. Therefore, the concentration of the PuEDTA species is dependent not only on the concentration of inorganic plutonium species but also on the concentration of inorganic iron species. The inorganic and organic chemical species of importance are in Table A-1 of the appendix.

2. The inorganic iron species are controlled by a specific iron mineral. Ferrosic oxide $[\text{Fe}_2(\text{OH})_2]$ is probably that mineral under conditions of reduction-oxidation cycles or under conditions of partial oxidation when highly reduced systems are exposed to more oxidized systems. The presence of silica or organic anions may inhibit the transformation of the metastable $\text{Fe}_2(\text{OH})_2$ to more crystalline, less soluble oxides.⁴ However, soil iron hydroxide $[\text{Fe}(\text{OH})_3]$ and magnetite (Fe_3O_4) are much less soluble and should eventually precipitate, causing $\text{Fe}_2(\text{OH})_2$ to dissolve. Magnetite is more stable at $\log (\text{Fe}^{2+}) + 2\text{-pH}$ greater than 4 and $\text{Fe}(\text{OH})_3$ (soil) is more stable at $\log (\text{Fe}^{2+}) + 2\text{-pH}$ less than about 4. Goethite ($\alpha\text{-FeOOH}$) and lepidocrocite ($\gamma\text{-FeOOH}$) crystallize rapidly at pH less than 6.⁴
3. Quantitative values of Eh can best be estimated from the concentrations of iron species in solution and from the stability of the iron solid controlling those concentrations.⁷ Eh measurements using a platinum electrode are only of value in showing trends.
4. For short term equilibration times, as in the case of laboratory experiments, the Eh for the plutonium system may be different from that for the iron system.⁷ In such instances, two Eh values need to be evaluated.

The derivations of the variable parameters needed in the thermodynamic evaluation of the influence of soil chemistry are outlined in the appendix. The variable parameters are soluble plutonium, soluble EDTA, Eh, pH, and EC. The various plutonium species can be expressed relative to one another in terms of pH, Eh, noncomplexed EDTA concentration, and stability constants; the concentration of soluble plutonium permits the calculation of absolute concentrations of the various plutonium species. In a similar manner, the concentration of soluble EDTA permits the calculation of absolute concentrations of the various EDTA species. Electrical conductivity is used to estimate ionic strength,⁸ which in turn is used to estimate the activity coefficients of specific species; activity coefficients relate thermodynamic concentrations to measured concentrations. The derivations may be expressed in a number of ways, depending on the information required. Those expressions are included in the appendix.

III. RESULTS AND DISCUSSION

A. Laboratory Experiments

In the first of the two laboratory experiments, three aliquots of anoxic Trench 19S waste were spiked with 2.1×10^{-6} moles/l plutonium and then allowed to equilibrate under oxic laboratory conditions; Waste 1 was equilibrated for approximately 1 hour, Waste 2 for 5 days, and Waste 3 for 6 days. At the end of each equilibration period a waste aliquot was centrifuged and the soluble characteristics of the waste determined (Table I). In each case a substantial amount of plutonium had been removed by centrifugation indicating precipitation of plutonium during equilibration under oxic laboratory conditions. An IAP for the precipitate, $\text{Pu}(\text{OH})_4$, was evaluated and compared with the K_{sp} of $\text{Pu}(\text{OH})_4$ found in the literature. The $\text{IAP}_{\text{Pu}(\text{OH})_4}$ is equal to $(\text{Pu}^{4+})(\text{OH}^-)^4$ and is the same as the K_{sp} $\text{Pu}(\text{OH})_4$ in the presence of the precipitate under equilibrium conditions. The OH^- concentration was determined from the measurement of the pH, and the Pu^{4+} concentration was calculated from estimated chemical parameters derived from analyses given in Table I and from thermodynamic relations presented in the appendix. The estimated chemical parameters and the calculated $\text{IAP}_{\text{Pu}(\text{OH})_4}$ are given in Table IV. A comparison of the $\text{IAP}_{\text{Pu}(\text{OH})_4}$ with the K_{sp} $\text{Pu}(\text{OH})_4$ indicates good agreement for 2 of the 3 waste aliquots (Waste 2 and Waste 3). In those two systems, the $\text{IAP}_{\text{Pu}(\text{OH})_4}$ was within a factor of 3 of the K_{sp} $\text{Pu}(\text{OH})_4$;⁹ in the third system (Waste 1), they differed by an order of magnitude. That difference is not excessive and is attributed to a general phenomenon usually observed during precipitation of solids; initially the solubility of the precipitate is usually less than that observed under equilibrium conditions. Waste 1 was equilibrated for only about 1 hour before the soluble characteristics were determined. The above results suggest that the use of thermodynamic relations in estimating concentrations of analytically nondetectable species of plutonium yield relatively good estimates of those concentrations.

TABLE IV

ESTIMATED CHEMICAL PARAMETERS OF SPIKED MAXEY FLATS TRENCH 19S
WASTE EQUILIBRATED UNDER OXIC LABORATORY CONDITIONS

	Waste 1	Waste 2	Waste 3
PuEDTA	3.4×10^{-9}	1.4×10^{-8}	2.1×10^{-8}
Inorganic Pu	1.1×10^{-10}	6.0×10^{-10}	6.6×10^{-10}
FeEDTA	1.3×10^{-5}	1.2×10^{-5}	1.4×10^{-5}
Inorganic Fe	3.9×10^{-6}	5.1×10^{-6}	6.0×10^{-6}
[Fe ²⁺]	4.1×10^{-7}	4.3×10^{-7}	3.4×10^{-7}
Eh Fe (mV)	77	44	4
[Fe ³⁺]	7.4×10^{-19}	2.2×10^{-19}	3.5×10^{-20}
[FeEDTA ⁻]	2.5×10^{-6}	9.5×10^{-7}	1.6×10^{-7}
[PuEDTA ⁻]/[Pu ³⁺]	4.3×10^5	5.5×10^5	5.8×10^5
Eh Pu (mV)	290	290	260
[Pu ⁴⁺]	5.4×10^{-26}	2.0×10^{-25}	5.2×10^{-26}
IAP Pu(OH) ₄	7.8×10^{-52}	9.8×10^{-51}	1.7×10^{-50}
K _{sp} Pu(OH) ₄	6.3×10^{-51}	6.3×10^{-51}	6.3×10^{-51}

In the second laboratory experiment, aliquots of the spiked waste were added to the Ap and C soils of the Tilsit series and equilibrated for 5 and 6 days, respectively. After equilibration, the systems were centrifuged and the characteristics of the soluble fraction determined (Table II). In the case of the spiked-waste/soil systems, the concentration of soluble plutonium was considerably less than that in the presence of the Pu(OH)₄ precipitate; the probable mechanism of plutonium removal from solution is by ion exchange. According to Nelson et al.,⁶ the adsorption of inorganic Pu(III,IV) exceeds the adsorption of inorganic species of oxidized plutonium [Pu(V,VI)]. For example, the K_d values of inorganic Pu(III,IV) are about 10⁶ mL/g for a wide range of environmental waters; the K_d values of inorganic Pu(V,VI) are less than 10³ for the same systems. The K_d of Pu(III,IV) will be lower in the presence of organic complexers because the organically complexed species of plutonium do not sorb. Under those conditions, as in the case of the Trench 19S waste, the inorganic Pu(III,IV) usually cannot be analytically measured because the concentration of the organic Pu(III,IV) greatly exceeds that of the inorganic Pu(III,IV); the two types of species are not differentiated in the analyses. However, inorganic Pu(III,IV) concentrations can be evaluated through thermodynamic analyses.

In the laboratory spiked waste/soil experiment, the concentration of the inorganic Pu(III,IV) was estimated from the analytical measurements given in Table II and from thermodynamic relations (see Appendix). The K_d values for the inorganic Pu(III,IV) were calculated and compared with those quoted by Nelson et al.⁶ and with those calculated from field experiments at the Maxey Flats burial site. Table V lists the chemical parameters estimated from analytical measurements and from thermodynamic relations. The PuEDTA concentration is estimated from the anionic and neutral fractions of measured plutonium; the FeEDTA concentration is estimated from the anionic fraction of measured iron. Also, the inorganic concentration of plutonium is estimated from the cation fraction of measured plutonium and the inorganic concentration of iron is estimated from the cationic and neutral fractions of measured iron. Other parameters are based on the above estimated organic and inorganic concentrations and

TABLE V

ESTIMATED CHEMICAL PARAMETERS OF SPIKED MAXEY FLATS
TRENCH 19S WASTE-TILSIT SOIL SYSTEMS

	Tilsit Ap	Tilsit C
PuEDTA	$(2.1 \pm 0.5) \times 10^{-9}$	$(2.2 \pm 1.1) \times 10^{-10}$
Inorganic Pu	$(6.3 \pm 2.1) \times 10^{-11}$	$(9.6 \pm 4.8) \times 10^{-11}$
FeEDTA	6.9×10^{-6}	2.59×10^{-6}
Inorganic Fe	4.0×10^{-6}	2.26×10^{-6}
$[\text{Fe}^{2+}]$	1.4×10^{-6}	1.3×10^{-6}
$[\text{e}^-]$ (V)	1.6×10^{-4}	5.1×10^{-7}
Eh Fe (V)	0.23	0.37
$[\text{Fe}^{3+}]$	8.3×10^{-16}	2.2×10^{-13}
$[\text{FeEDTA}^-]$	5.5×10^{-6}	2.2×10^{-6}
$[\text{PuEDTA}^-]/[\text{Pu}^{3+}]$	8.3×10^2	1.3
Eh Pu (V)	0.31	0.33
$[\text{Pu}^{4+}]$	4.6×10^{-23}	6.0×10^{-21}
$[\text{Pu}^{3+}]$	2.0×10^{-12}	1.2×10^{-10}
$[\text{PuOH}^{2+}]$	8.1×10^{-13}	1.3×10^{-11}
$[\text{PuO}_2^+]$	6.5×10^{-11}	7.2×10^{-11}
Inorganic Pu (calculated)	6.8×10^{-11}	2.1×10^{-10}
PuEDTA (calculated)		
% Anionic	90	80
% Neutral	10	20
Pu sorbed (moles/g)	8.56×10^{-9}	8.56×10^{-9}
K_d Pu(III,IV) (mL/g)	3.1×10^6	6.1×10^4

NOTE: Concentrations expressed as moles/L unless noted.

thermodynamic relations. The concentration of adsorbed plutonium is based on the concentration of plutonium added to the system and the concentration of measured soluble plutonium.

The results of the above calculations indicate a K_d for inorganic Pu(III,IV) of 3×10^6 for the Ap soil and 6×10^4 for the C soil when each was interacted with the spiked Trench 19S waste. The K_d for the Ap soil compares favorably with those previously quoted by Nelson et al.⁶ The K_d for the C soil is about an order of magnitude lower. Even though the K_d for the C soil is somewhat lower than for other quoted K_d values, it does not appear to be unrealistic. The C soil should be comparable to the deeper soil at the Trench 19S study area at the Maxey Flats site. Distribution coefficients for the inorganic Pu(III,IV) are evaluated for the field experiment in the next section. Similar K_d values calculated under different conditions, as in field experiments, will lend support to thermodynamic evaluations.

B. Field Experiment

In the field experiment, porous ceramic cup samplers were implanted in the soil near Trench 19S in a horizontal and vertical array. Soil solutions were collected and analyzed for their chemical characteristics. Trench 19S waste was also collected through a porous cup sampler and analyzed in a similar manner. Analytical measurements of waste and soil characteristics (Table III) and thermodynamic relations were used to calculate the inorganic Pu(III,IV). The soil collected during the implantation of the porous cup sampler was also analyzed for plutonium. Based on those analyses and the calculated inorganic Pu(III,IV) concentrations, K_d values were calculated for each of the three soil locations. Those results are given in Table VI. The iron minerals that were assumed to control the inorganic concentration of iron are also given in Table VI. The basis for selecting the particular iron mineral is given in Sec II.C. Two values of plutonium concentration (less than and greater than or equal to) are given for the two locations farthest from the trench. Both ^{238}Pu and $^{239,240}\text{Pu}$ were present in the waste and soil solutions. However, at those two locations, the concentration of $^{239,240}\text{Pu}$ was below analytical detection and the concentration of ^{238}Pu was analytically identified and measured. Thus, the less than value represents the detection limit for $^{239,240}\text{Pu}$ and the greater than or equal to concentration represents the measured concentration of ^{238}Pu . Similarly, greater than and less than or equal to values are presented for the calculated K_d values at those two locations for the same reasons.

The calculated K_d values for the three soil locations appear to be comparable. The K_d for the soil location 1.5 m from the trench may be in error because at the time the porous cup sampler was implanted, the soil was collected before an apparent fracture was breached. As a result, the soil solution collected by the porous cup may contain more plutonium than the solution in contact with the soil before the soil sample was collected. If in error, the actual K_d is probably greater than that calculated. The K_d

TABLE VI
CONCENTRATIONS AND DISTRIBUTION COEFFICIENTS OF INORGANIC
Pu(III,IV) IN TRENCH WASTE, SOIL SOLUTIONS, AND SOILS FROM
THE TRENCH 19S STUDY AREA OF THE MAXEY FLATS BURIAL FACILITY

	Trench Waste	Soil Solutions		
		Approximate Distance from Trench (m)		
		1.5	3.0	6.0
Soluble EDTA (moles/L)	2.2×10^{-4}	8.1×10^{-5}	6.1×10^{-7}	3.4×10^{-6}
Soluble Pu (moles/L)	1.53×10^{-11}	4.75×10^{-13}	$<6.14 \times 10^{-14}$ $\geq 7.6 \times 10^{-16}$	$<6.4 \times 10^{-14}$ $\geq 2.2 \times 10^{-15}$
Fe Mineral	Fe_3O_4	Fe_3O_4	$\text{Fe}_3(\text{OH})_8$	$\gamma\text{-FeOOH}$
Eh(V) Calculated	-0.30	-0.18	0.37	0.13
pH	7.25	6.80	6.30	5.60
EC (dS/m)	1.55	1.41	3.10	3.30
Inorganic Pu(III,IV) (moles/mL)	8.9×10^{-19}	3.6×10^{-20}	$<4.8 \times 10^{-19}$ $\geq 5.7 \times 10^{-20}$	$<3.8 \times 10^{-19}$ $\geq 1.3 \times 10^{-20}$
Sorbed Pu (moles/g soil)	-	2.0×10^{-16}	2.13×10^{-15}	5.65×10^{-16}
K_d Inorganic Pu(III,IV) (mL/g)	-	5.6×10^3	$>4.4 \times 10^2$ $\leq 3.7 \times 10^4$	$>1.5 \times 10^3$ $\leq 4.3 \times 10^4$

values in Table VI are also comparable to the K_d values calculated for the Tilsit C soil in the laboratory experiment. The similarities in those calculated K_d values suggest that the method of evaluation of inorganic Pu(III,IV) is realistic.

C. Soil Chemistry Effects

The results of the evaluation of an IAP for $\text{Pu}(\text{OH})_4$ in the waste system and the evaluation of K_d values for inorganic Pu(III,IV) sorbed to soil suggest that the use of thermodynamic relations for modeling of the influence of soil chemistry on the mobility of PuEDTA is realistic and feasible. Thus, the thermodynamic relations and the analytically determined characteristics of the waste and soil solutions are used to evaluate the differences in the solution chemistry between the waste trench and the nearby soil that affect the mobility of PuEDTA. Chemical parameters estimated for that evaluation are given in Table VII. With the exception of the oxidized species of inorganic plutonium and iron, concentrations are lower in the soil solutions than in the waste. That decrease, in part, may be attributed to the dilution of the waste with soil water as the waste moves into the nearby soil environment. Thus, to compare data from

TABLE VII
ESTIMATED CONCENTRATIONS OF IRON AND PLUTONIUM SPECIES IN
TRENCH WASTE AND SOIL SOLUTIONS FROM THE TRENCH 19S
STUDY AREA OF THE MAXEY FLATS BURIAL FACILITY

	Trench Waste	Soil Solutions		
		Approximate Distance from Trench (m)		
		1.5	3.0	6.0
Fe Mineral	Fe_3O_4	Fe_3O_4	$\text{Fe}_3(\text{OH})_8$	$\gamma\text{-FeOOH}$
Eh(V) Calculated	-0.30	-0.28	0.37	0.13
pH	7.25	6.80	6.30	5.60
FeEDTA	2.2×10^{-4}	8.1×10^{-5}	6.1×10^{-7}	3.4×10^{-6}
% Reduced	100	100	4	20
% Oxidized	0	0	96	80
Inorganic Fe Calculated	4.9×10^{-4}	1.9×10^{-4}	1.9×10^{-6}	5.9×10^{-5}
Reduced	4.9×10^{-4}	1.9×10^{-4}	1.2×10^{-6}	5.9×10^{-5}
Oxidized	8.1×10^{-14}	5.7×10^{-13}	6.5×10^{-7}	6.0×10^{-12}
PuEDTA	1.53×10^{-11}	4.7×10^{-13}	$<2.0 \times 10^{-15}$ $\geq 2.5 \times 10^{-17}$	$<6.4 \times 10^{-14}$ $\geq 2.2 \times 10^{-15}$
Inorganic Pu Calculated	8.9×10^{-16}	3.6×10^{-17}	$<5.9 \times 10^{-14}$ $\geq 7.4 \times 10^{-16}$	$<3.8 \times 10^{-16}$ $\geq 1.3 \times 10^{-17}$
Reduced	8.9×10^{-16}	3.6×10^{-17}	$<4.6 \times 10^{-15}$ $\geq 5.7 \times 10^{-17}$	$<3.8 \times 10^{-16}$ $\geq 1.3 \times 10^{-17}$
Oxidized	7.1×10^{-32}	2.1×10^{-32}	$<5.5 \times 10^{-14}$ $\geq 6.8 \times 10^{-16}$	$<8.4 \times 10^{-26}$ $\geq 2.9 \times 10^{-27}$
[EDTA ⁴⁻]	1.8×10^{-16}	9.6×10^{-17}	2.3×10^{-17}	1.5×10^{-18}

Concentrations are expressed as moles/L.

the trench waste with those in the soil solution, the concentrations of interest are normalized with respect to EDTA, FeEDTA, or PuEDTA. Those results are given in Table VIII.

The concentration of PuEDTA relative to the total EDTA concentration is less in the soil solutions than in the trench waste and that difference indicates that factors other than waste dilution by soil water play an important role in reducing the concentration of the plutonium complex. The concentration of inorganic Fe(II) in the soil solutions tends to be about the same or slightly higher than that in the trench waste; the concentration of inorganic Fe(III) is much higher and that of EDTA^{4-} is less. The data in Table VII indicate that the FeEDTA species are predominantly Fe(II) species in and very near the trench, whereas they are predominantly Fe(III) species in the soil solutions farther from the trench. The above observations suggest that the inorganic species of iron, because of their increased concentration, react with the EDTA^{4-} ligand to form more of the FeEDTA complex to maintain an equilibrium with respect to that reaction. As a result, the concentration of EDTA^{4-} ligand should decrease relative to that of FeEDTA. The net concentration of the inorganic iron species should not decrease as a result of that reaction because the inorganic iron species are controlled by the iron mineral in the soil.

The data in Table VIII also indicate increases in concentrations of EDTA^{4-} and inorganic plutonium relative to that of the PuEDTA complex when their concentrations in the soil solutions are compared with their concentrations in the trench waste. Those observations suggest that as a result of a decrease in the EDTA^{4-} ligand concentration, because of its reaction with inorganic iron, the PuEDTA dissociates in order to maintain an equilibrium for the Pu^{3+} - EDTA^{4-} reaction. As a result, the concentrations of both Pu^{3+} and EDTA^{4-} relative to the concentration of PuEDTA should be greater in the soil solutions than in the trench waste. An increase in sorption should also occur because the Pu^{3+} concentration increases on dissociation of PuEDTA; Pu(III,IV) species are the species that tend to be sorbed by soils. The increase in sorption reduced the Pu^{3+} concentration, thus resulting in further dissociation of the PuEDTA complex until equilibrium is established for both the dissociation and sorption reactions.

TABLE VIII

RELATIVE CONCENTRATIONS OF IRON AND PLUTONIUM SPECIES IN
TRENCH WASTE AND SOIL SOLUTIONS FROM THE TRENCH 19S STUDY AREA
OF THE MAXEY FLATS BURIAL FACILITY

	Trench Waste	Soil Solutions		
		Approximate Distance from Trench (m)		
		1.5	3.0	6.0
EDTA (mole/L)	2.2×10^{-4}	8.1×10^{-5}	1.8×10^{-6}	1.0×10^{-5}
PuEDTA	7.0×10^{-8}	5.8×10^{-9}	$\leq 3.3 \times 10^{-9}$	$\leq 1.9 \times 10^{-8}$
EDTA			$> 4.1 \times 10^{-11}$	$> 6.5 \times 10^{-10}$
Inorganic Fe(II)	2.2	2.3	3.0	17
FeEDTA				
Inorganic Fe(III)	3.7×10^{-10}	7.0×10^{-8}	1.1	6.0×10^{-7}
FeEDTA				
[EDTA^{4-}]	8.2×10^{-13}	1.2×10^{-12}	3.2×10^{-15}	4.4×10^{-13}
FeEDTA				
[EDTA^{4-}]	1.2×10^{-5}	2.0×10^{-4}	$> 1 \times 10^{-6}$	$> 2.3 \times 10^{-5}$
PuEDTA			$\leq 7.9 \times 10^{-5}$	$\leq 6.8 \times 10^{-4}$
Inorganic Pu	5.8×10^{-5}	7.7×10^{-5}	30	6.0×10^{-3}
PuEDTA				

IV. SUMMARY AND CONCLUSIONS

Laboratory and field experiments were conducted to evaluate the feasibility of thermodynamically modeling the behavior of organically complexed plutonium and to evaluate the effects of changes in soil chemistry on the stability (mobility) of PuEDTA. In the laboratory, thermodynamic considerations were used to calculate the $IAP_{Pu(OH)_4}$ for a plutonium precipitate in a spiked Maxey Flats trench waste. That $IAP_{Pu(OH)_4}$ is in good agreement with the $K_{spPu(OH)_4}$ given in the literature. Distribution coefficients were determined in laboratory and field experiments on the basis of the concentration of the inorganic Pu(III,IV) in soil solutions; those concentrations were evaluated from analytical measurements and thermodynamic considerations. Good agreement was obtained between K_d values from laboratory experiments and those from field experiments. Also, those K_d values are in reasonable agreement with those evaluated elsewhere.

The effect of soil chemistry on the stability (mobility) of PuEDTA at the Maxey Flats burial site is summarized as pertinent reactions (Table IX). As the waste moves into the soil environment, the inorganic iron species increase; those species interact with the $EDTA^{4-}$ species to form more FeEDTA, thus decreasing the $EDTA^{4-}$ concentration. That decrease results in a dissociation of the PuEDTA species, thus increasing the concentration of sorbable plutonium species. The sorption of those species reduces their concentration in the solution, thus resulting in an additional dissociation of the PuEDTA until equilibrium is established for both the dissociation and sorption reactions.

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TABLE IX
REACTIONS SUMMARIZING THE INFLUENCE OF SOIL CHEMISTRY
ON THE MOBILITY OF PuEDTA

Reaction Number	Reaction
1	$Fe_3O_4 + 8H^+ + 2e^- \rightleftharpoons 3Fe^{2+} + 4H_2O$
2	$Fe_3O_4 + 8H^+ \rightleftharpoons 3Fe^{3+} + e^- + 4H_2O$
3	$Fe^{2+} + EDTA^{4-} \rightleftharpoons FeEDTA^{2-}$
4	$Fe^{3+} + EDTA^{4-} \rightleftharpoons FeEDTA^-$
5	$Pu^{3+} + EDTA^{4-} \rightleftharpoons PuEDTA^-$
6	$Pu^{3+} + Soil \rightleftharpoons Pu \cdot Soil$

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APPENDIX

BASIC EQUATIONS AND THE DERIVATION OF VARIABLE PARAMETERS NEEDED FOR THE THERMODYNAMIC INTERPRETATION OF THE INFLUENCE OF SOIL CHEMISTRY ON THE MOBILITY (STABILITY) OF PuEDTA

The variable parameters needed for the thermodynamic interpretation of the influence of soil chemistry on the mobility (stability) of PuEDTA are derived from basic equations that describe the relative concentrations of plutonium and iron species in waste and soil systems. Those basic thermodynamic equations are given in Table A-1.

The concentration of soluble plutonium can be described as the sum of the concentrations of organic and inorganic plutonium species.

$$m_{\text{sol Pu}} = m_{\text{org Pu}} + m_{\text{inorg Pu}} \quad (1)$$

where m is the molality of the respective plutonium species.

Assuming EDTA is the controlling organic,

$$m_{\text{org Pu}} = \sum m_{\text{PuEDTA species}} \quad (2)$$

$$m_{\text{org Pu}} = m_{\text{PuEDTA}^0} + m_{\text{PuEDTA}^-} + m_{\text{PuO}_2\text{EDTA}^{3-}} + m_{\text{PuO}_2\text{EDTA}^{2-}} + m_{\text{PuOHEDTA}^-} \quad (3)$$

Substitution of thermodynamic concentration for molality gives

$$m_{\text{org Pu}} = \frac{[\text{Pu EDTA}^0]}{\gamma_{\text{Pu EDTA}^0}} + \frac{[\text{Pu EDTA}^-]}{\gamma_{\text{Pu EDTA}^-}} + \frac{[\text{PuO}_2\text{EDTA}^{3-}]}{\gamma_{\text{PuO}_2\text{EDTA}^{3-}}} + \frac{[\text{PuO}_2\text{EDTA}^{2-}]}{\gamma_{\text{PuO}_2\text{EDTA}^{2-}}} + \frac{[\text{PuOH EDTA}^-]}{\gamma_{\text{Pu OHEDTA}^-}} \quad (4)$$

where $[]$ indicates chemical activity (thermodynamic concentration) and γ indicates activity coefficient of the respective species. Equation (4) can be expressed in terms of $[\text{Pu}^{4+}]$, $[\text{EDTA}^{4-}]$, and a constant

$$m_{\text{org Pu}} = [\text{Pu}^{4+}][\text{EDTA}^{4-}] K_1(\text{pH}, \text{Eh}) \quad (5)$$

where K_1 is dependent on pH and Eh. K_1 is given in Table A-2. The various components of K_1 are derived from equations given in Table A-1.

The concentration of inorganic Pu can be expressed as the sum of individual species

$$m_{\text{inorg Pu}} = m_{\text{Pu}^{4+}} + m_{\text{Pu}^{3+}} + m_{\text{PuO}_2^+} + m_{\text{PuO}_2^0} + m_{\text{PuOH}^{3+}} + m_{\text{PuOH}^{2+}} \quad (6)$$

$$m_{\text{inorg Pu}} = \frac{[\text{Pu}^{4+}]}{\gamma_{\text{Pu}^{4+}}} + \frac{[\text{Pu}^{3+}]}{\gamma_{\text{Pu}^{3+}}} + \frac{[\text{PuO}_2^+]}{\gamma_{\text{PuO}_2^+}} + \frac{[\text{PuO}_2^{2+}]}{\gamma_{\text{PuO}_2^{2+}}} + \frac{[\text{PuOH}^{3+}]}{\gamma_{\text{PuOH}^{3+}}} + \frac{[\text{PuOH}^{2+}]}{\gamma_{\text{PuOH}^{2+}}} \quad (7)$$

Equation (7) can be expressed in terms of $[\text{Pu}^{4+}]$ and a constant.

$$m_{\text{inorg Pu}} = [\text{Pu}^{4+}] K_2(\text{pH}, \text{Eh}) \quad (8)$$

where K_2 is dependent on pH and Eh. K_2 is given in Table A-2. The various components of K_2 are derived from equations given in Table A-1.

The concentration of soluble iron can also be described as the sum of the concentrations of organic and inorganic species.

$$m_{\text{sol Fe}} = m_{\text{org Fe}} + m_{\text{inorg Fe}} \quad (9)$$

where

$$m_{\text{org Fe}} = m_{\text{FeEDTA}^-} + m_{\text{FeOHEDTA}^{2-}} + m_{\text{FeEDTA}^{2-}} + m_{\text{FeOHEDTA}^{3-}} + m_{\text{FeHEDTA}^-} \\ + m_{\text{Fe(OH)}_2\text{EDTA}^{4-}} + m_{\text{Fe(OH)}_2\text{EDTA}^{3-}} \quad (10)$$

Substitution of thermodynamic concentration for molality gives

$$m_{\text{org Fe}} = \frac{[\text{FeEDTA}^-]}{\gamma_{\text{FeEDTA}^-}} + \frac{[\text{FeOHEDTA}^{2-}]}{\gamma_{\text{FeOHEDTA}^{2-}}} + \frac{[\text{FeEDTA}^{2-}]}{\gamma_{\text{FeEDTA}^{2-}}} + \frac{[\text{FeOHEDTA}^{3-}]}{\gamma_{\text{FeOHEDTA}^{3-}}} \\ + \frac{[\text{FeHEDTA}^-]}{\gamma_{\text{FeHEDTA}^-}} + \frac{[\text{Fe(OH)}_2\text{EDTA}^{4-}]}{\gamma_{\text{Fe(OH)}_2\text{EDTA}^{4-}}} + \frac{[\text{Fe(OH)}_2\text{EDTA}^{3-}]}{\gamma_{\text{Fe(OH)}_2\text{EDTA}^{3-}}} \quad (11)$$

Equation (11) can be expressed in terms of $[\text{Fe}^{3+}][\text{EDTA}^{4-}]$ and a constant

$$m_{\text{org Fe}} = [\text{EDTA}^{4-}][\text{Fe}^{3+}] K_3(\text{pH}, \text{Eh}) \quad (12)$$

where K_3 is dependent on pH and Eh. K_3 is given in Table A2. The various components of K_3 are derived from equations given in Table A-1.

The concentration of inorganic species can be expressed in terms of the concentrations of oxidized species, Fe(III), and reduced species, Fe(II).

$$m_{\text{inorg Fe}} = m_{\text{inorg Fe(III)}} + m_{\text{inorg Fe(II)}} \quad (13)$$

where

$$m_{\text{inorg Fe(III)}} = m_{\text{Fe}^{3+}} + m_{\text{FeOH}^{2+}} + m_{\text{Fe(OH)}_2^+} + m_{\text{Fe(OH)}_3^0} \quad (14)$$

Substitution of thermodynamic concentrations for molalities gives

$$m_{\text{inorg Fe(III)}} = \frac{[\text{Fe}^{3+}]}{\gamma_{\text{Fe}^{3+}}} + \frac{[\text{FeOH}^{2+}]}{\gamma_{\text{FeOH}^{2+}}} + \frac{[\text{Fe(OH)}_2^+]}{\gamma_{\text{Fe(OH)}_2^+}} + \frac{[\text{Fe(OH)}_3^0]}{\gamma_{\text{Fe(OH)}_3^0}} \quad (15)$$

Equation (15) can be expressed in terms of (Fe^{3+}) and a constant

$$m_{\text{inorg Fe(III)}} = [\text{Fe}^{3+}] K_4(\text{pH}) \quad (16)$$

where K_4 is dependent on only pH. K_4 is given in Table A-2. The various components of K_4 are derived from equations given in Table A-1.

The molality of the reduced inorganic iron species can be expressed as

$$m_{\text{inorg Fe(II)}} = m_{\text{Fe}^{2+}} + m_{\text{FeOH}^+} + m_{\text{Fe(OH)}_2^0} \quad (17)$$

Substitutions of thermodynamic concentration for molality gives

$$m_{\text{inorg Fe(II)}} = \frac{[\text{Fe}^{2+}]}{\gamma_{\text{Fe}^{2+}}} + \frac{[\text{FeOH}^+]}{\gamma_{\text{FeOH}^+}} + \frac{\text{Fe(OH)}_2^0}{\gamma_{\text{Fe(OH)}_2^0}} \quad (18)$$

Equation (18) can be expressed in terms of $[\text{Fe}^{2+}]$ and a constant

$$m_{\text{inorg Fe(II)}} = [\text{Fe}^{2+}] K_5(\text{pH}) \quad (19)$$

where K_5 is dependent on pH. K_5 is given in Table A-2. The various components of K_5 are derived from equations in Table A-1.

In general, $m_{\text{Fe(II)}} \gg \gg m_{\text{Fe(III)}}$ such that

$$[\text{Fe}^{2+}] = \frac{m_{\text{inorg Fe}}}{K_5(\text{pH})} \quad (20)$$

The $m_{\text{inorg Fe}}$ can be estimated from the cationic and neutral fractions of the measured concentrations of soluble iron. Thus, $[\text{Fe}^{2+}]$ can be calculated.

Under short term equilibrations such as in the laboratory experiments where $\text{Fe}_3(\text{OH})_4$ controls the concentration of $[\text{Fe}^{2+}]$, Eh can be calculated as follows

$$\text{Eh} = \text{pe} (59.2); \text{pe} = -\log [e^-] \quad (21)$$

where

$$[e^-]^2 = \frac{10^{43.75} [\text{Fe}^{2+}]^3}{[\text{H}^+]^8} \quad (22)$$

$[\text{Fe}^{3+}]$ is related to $[\text{Fe}^{2+}]$ and Eh as given in equation (23).

$$[\text{Fe}^{3+}] = 10^{-13.04} [\text{Fe}^{2+}] 10^{\text{Eh}/0.0592} \quad (23)$$

Under long term equilibrations, the iron mineral controlling $[\text{Fe}^{3+}]$ is lepidocrocite ($\gamma\text{-FeOOH}$) such that

$$[\text{Fe}^{3+}] = 10^{1.39} [\text{H}^+]^3 \quad (24)$$

Under these long term equilibration conditions, the Eh can be calculated from equation (23); $[\text{Fe}^{2+}]$ is known from equation (20) and $[\text{Fe}^{3+}]$ from equation (24).

$[\text{EDTA}^{4-}]$ can be expressed in terms of the species $[\text{FeEDTA}^-]$ and $[\text{Fe}^{3+}]$.

$$[\text{EDTA}^{4-}] = \frac{[\text{FeEDTA}^-]}{[\text{Fe}^{3+}]} 10^{-27.59} \quad (25)$$

Equation (25) can be substituted into equation (12) such that

$$m_{\text{org Fe}} = [\text{FeEDTA}^-] 10^{-27.59} K_3(\text{pH}, \text{Eh}) \quad (26)$$

Rearranging equation (26)

$$[\text{FeEDTA}^-] = \frac{m_{\text{org Fe}}}{10^{-27.59} K_3(\text{pH}, \text{Eh})} \quad (27)$$

where Eh has been calculated for the iron system and $m_{\text{org Fe}}$ is the anionic fraction of soluble iron.

$[\text{EDTA}^{4-}]$ can also be expressed in terms of $[\text{PuEDTA}^-]$ and $[\text{Pu}^{3+}]$ species.

$$[\text{EDTA}^{4-}] = \frac{[\text{PuEDTA}^-]}{[\text{Pu}^{3+}]} 10^{-20.69} \quad (28)$$

Substituting equation (28) into equation (5)

$$m_{\text{org Pu}} = [\text{Pu}^{4+}] \frac{[\text{PuEDTA}^-]}{[\text{Pu}^{3+}]} 10^{-20.69} K_1(\text{pH}, \text{Eh}) \quad (29)$$

$[\text{PuEDTA}^-]$ can be calculated from equation (30)

$$\frac{[\text{PuEDTA}^-]}{[\text{Pu}^{3+}]} = \frac{[\text{FeEDTA}^-]}{[\text{Fe}^{3+}]} 10^{-6.90} \quad (30)$$

Then equations (8) and (29) can be equated through $[\text{Pu}^{4+}]$. Under those conditions, the one unknown is Eh for the plutonium system, which can then be calculated. That method of calculating Eh is used under short term equilibration periods where the Eh of the iron system is different from that of the plutonium system. The constants based on that calculated Eh can then be substituted into either equation (8) or equation (29) and $[\text{Pu}^{4+}]$ calculated. The thermodynamic concentration of Pu^{4+} can also be calculated by substituting equation (12) into equation (5).

Under long term equilibration periods, $[\text{Pu}^{4+}]$ can be estimated from equation (8) when $m_{\text{inorg Pu}}$ is known. When soluble plutonium, soluble EDTA, pH, and Eh are known, $[\text{Pu}^{4+}]$ can also be estimated as follows.

Soluble plutonium is the sum of equations (5) and (8).

$$m_{\text{sol Pu}} = [\text{Pu}^{4+}] [\text{EDTA}^{4-}] K_1(\text{pH}, \text{Eh}) + [\text{Pu}^{4+}] K_2(\text{pH}, \text{Eh}) \quad (31)$$

Soluble EDTA is the sum of equations (5) and (12).

$$m_{\text{sol EDTA}} = [\text{Pu}^{4+}] [\text{EDTA}^{4-}] K_1(\text{pH}, \text{Eh}) + [\text{EDTA}^{4-}] [\text{Fe}^{3+}] K_3(\text{pH}, \text{Eh}) \quad (32)$$

$[\text{EDTA}^{4-}]$ derived from equation (32) can be substituted into equation (31) such that $[\text{Pu}^{4+}]$ can be calculated by solving a quadratic equation.

TABLE A-1

**BASIC REACTIONS CONSIDERED IN THE THERMODYNAMIC INTERPRETATION
OF THE INFLUENCE OF SOIL CHEMISTRY ON MOBILITY OF PuEDTA**

Reaction Number	Reaction	$\mu = 0.1$	$\mu = 0.0^a$	Reference
1	$\text{Pu}^{4+} + \text{EDTA}^{4-} = \text{PuEDTA}^0$	27.04	30.46	10,11
2	$\text{PuOH}^{3+} + \text{EDTA}^{4-} = \text{PuOHEDTA}^-$	17.66	20.23	10
3	$\text{Pu}^{3+} + \text{EDTA}^{4-} = \text{PuEDTA}^-$	18.12	20.69	10
4	$\text{PuO}_2^{2+} + \text{EDTA}^{4-} = \text{PuO}_2\text{EDTA}^{3-}$	10.18 ^b	10.86	11,12
5	$\text{PuO}_2^{2+} + \text{EDTA}^{4-} = \text{PuO}_2\text{EDTA}^{2-}$	16.39	18.10	11,13
6	$\text{Pu}^{3+} = \text{Pu}^{4+} + e^-$	—	15.91	14
7	$\text{PuO}_2^{2+} + 4\text{H}^+ + e^- = \text{Pu}^{4+} + 2\text{H}_2\text{O}$	—	20.00	14
8	$\text{PuO}_2^{2+} + 4\text{H}^+ + 2e^- = \text{Pu}^{4+} + 2\text{H}_2\text{O}$	—	35.69	14
9	$\text{PuOH}^{3+} + \text{H}^+ = \text{Pu}^{4+} + \text{H}_2\text{O}$	—	-1.10	14
10	$\text{PuOH}^{2+} + \text{H}^+ = \text{Pu}^{4+} + \text{H}_2\text{O} + e^-$	—	-8.72	14
11	$\text{Fe}^{3+} + \text{EDTA}^{4-} = \text{FeEDTA}^-$	25.10	27.59	9
12	$\text{FeEDTA}^- + \text{OH}^- = \text{FeOHEDTA}^{2-}$	6.45	6.13	9
13	$\text{Fe}^{3+} + \text{FeEDTA}^{2-} = \text{Fe}^{2+} + \text{FeEDTA}^-$	10.7	11.55	9
14	$\text{Fe}^{2+} + \text{EDTA}^{4-} = \text{FeEDTA}^{2-}$	14.2	15.91	9
15	$\text{FeEDTA}^{2-} + \text{H}^+ = \text{FeHEDTA}^-$	2.7	3.02	9
16	$\text{FeEDTA}^{2-} + \text{OH}^- = \text{FeOHEDTA}^{3-}$	4.8	4.27	9
17	$\text{FeOHEDTA}^{3-} + \text{OH}^- = \text{Fe}(\text{OH})_2\text{EDTA}^{4-}$	4.1	3.35	9
18	$\text{FeOHEDTA}^{2-} + \text{OH}^- = \text{Fe}(\text{OH})_2\text{EDTA}^{3-}$	4.53	4.10	9
19	$\text{Fe}^{3+} + \text{H}_2\text{O} = \text{FeOH}^{2+} + \text{H}^+$	—	-2.19	15
20	$\text{Fe}^{3+} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2^+ + 2\text{H}^+$	—	-5.69	15
21	$\text{Fe}^{3+} + 3\text{H}_2\text{O} = \text{Fe}(\text{OH})_3^0 + 3\text{H}^+$	—	-13.09	15
22	$\text{Fe}^{2+} + \text{H}_2\text{O} = \text{FeOH}^+ + \text{H}^+$	—	-6.74	15
23	$\text{Fe}^{2+} + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_2^0 + 2\text{H}^+$	—	-16.04	15
24	$\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$	—	13.04	15
25	$\text{Fe}_3(\text{OH})_4(\text{ferrosic oxide}) + 8\text{H}^+ + 2e^- = 3\text{Fe}^{2+} + 8\text{H}_2\text{O}$	—	43.75	15
26	$\text{Fe}_3\text{O}_4(\text{magnetite}) + 8\text{H}^+ + 2e^- = 3\text{Fe}^{2+} + 8\text{H}_2\text{O}$	—	35.69	15
27	$\gamma\text{FeOOH}(\text{lepidocrocite}) + 3\text{H}^+ = \text{Fe}^{3+} + 2\text{H}_2\text{O}$	—	1.39	15
28	$\text{Eh (mV)} = \text{pe}^- (59.2)$	—	—	15
29	$\mu (\text{moles/l}) = 0.013 \text{ EC (dS/m)}$	—	—	8

^aWhen log Keq at an ionic strength (μ) of 0.0 is not given in reference, it is calculated from Keq at $\mu = 0.1$ by the Davies equation.¹⁵

^bLog Keq is based on $\mu = 0.05$.

TABLE A-II

EQUATIONS RELATING THE RELATIVE CONTRIBUTION OF PLUTONIUM AND IRON SPECIES TO THEIR TOTAL CONCENTRATIONS

$$K_1(\text{pH}, \text{Eh}) = \left[\frac{10^{30.46}}{\gamma \text{PUEDTA}^0} + \frac{10^{36.57-C}}{\gamma \text{PuEDTA}^-} + \frac{10^{9.07+C}}{[\text{H}^+]^4 \gamma \text{PuO}_2 \text{EDTA}^{3-}} + \frac{10^{-16.36+2C}}{[\text{H}^+]^4 \gamma \text{PuO}_2 \text{EDTA}^{2-}} + \frac{10^{19.13}}{[\text{H}^+] \gamma \text{PuOHEDTA}^-} \right]$$

$$K_2(\text{pH}, \text{Eh}) = \left[\frac{1}{\gamma \text{Pu}^{4+}} + \frac{10^{15.88-C}}{\gamma \text{Pu}^{3+}} + \frac{10^{-19.93+C}}{[\text{H}^+]^4 \gamma \text{PuO}_2^+} + \frac{10^{-34.46+2C}}{[\text{H}^+]^4 \gamma \text{PuO}_2^{2+}} + \frac{10^{-1.10}}{[\text{H}^+] \gamma \text{PuOH}^{3+}} + \frac{10^{9.78-C}}{[\text{H}^+] \gamma \text{PuOH}^{2+}} \right]$$

$$K_3(\text{pH}, \text{Eh}) = \left[\frac{10^{27.59}}{\gamma \text{FeEDTA}^-} + \frac{10^{19.72}}{[\text{H}^+] \gamma \text{FeOHEDTA}^{2-}} + \frac{10^{28.95-C}}{\gamma \text{FeEDTA}^{2-}} + \frac{10^{19.22-C}}{[\text{H}^+] \gamma \text{FeOHEDTA}^{3-}} \right. \\ \left. + \frac{10^{0.15-C} [\text{H}^+]}{\gamma \text{FeHEDTA}^-} + \frac{10^{8.57-C}}{[\text{H}^+]^2 \gamma \text{Fe}(\text{OH})_2 \text{EDTA}^{4-}} + \frac{10^{9.82}}{[\text{H}^+]^2 \gamma \text{Fe}(\text{OH})_2 \text{EDTA}^{3-}} \right]$$

$$K_4(\text{pH}) = \left[\frac{1}{\gamma \text{Fe}^{3+}} + \frac{10^{-2.19}}{[\text{H}^+] \gamma \text{FeOH}^{2+}} + \frac{10^{-5.69}}{[\text{H}^+]^2 \gamma \text{Fe}(\text{OH})_2^+} + \frac{10^{-13.09}}{[\text{H}^+]^3} \right]$$

$$K_5(\text{pH}) = \left[\frac{1}{\gamma \text{Fe}^{2+}} + \frac{10^{-6.74}}{[\text{H}^+] \gamma \text{FeOH}^+} + \frac{10^{-16.04}}{[\text{H}^+]^2} \right]$$

where

$$C = \text{Eh}/0.0592$$

SECTION IV

STUDY OF UNSATURATED ZONE HYDROLOGY AT MAXEY FLATS

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STUDY OF UNSATURATED ZONE HYDROLOGY AT MAXEY FLATS

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ABSTRACT

The initial objective of this research was to determine the pathway(s) of water entry into the low-level radioactive waste burial trenches at Maxey Flats. The second objective is to investigate possible countermeasures for reducing water infiltration into the trenches. To investigate the pathway(s) of water entry, electrical soil moisture sensors and mini-porous cups were implanted in the trench cap of Trench 19S and in the soil profile adjacent to the trench. Relative soil moisture data is given from February 1980 through September 1982. Tritium present in the waste was employed as a tracer of water movement. It was found that the principal mode of water entry into the trench was by percolation through the trench cap and that lateral movement within the soil profile is very slow. It was also found that deep vertical movement of water through the undisturbed soil profile was very slow. The Kentucky fescue grass that has been grown on the site takes up significant tritium from the trenches and by transpiration transports the tritium to the atmosphere. Also, it was suggested that tritium in the plant transpiration stream might serve as a tool for mapping trench boundaries. A lysimeter experiment has been set up for the purpose of investigation of management countermeasures for reducing water infiltration into the trenches. Lysimeters, along with field plots, are being used to obtain quantitative determination of plant transport of tritium to the atmosphere.

INTRODUCTION

The problem of serious concern at Maxey Flats is the intrusion of excessive water into the waste burial trenches and the exit of that water while carrying radionuclides (1, 2, 3). This study was initiated to determine the principal pathways of water entry into the waste burial trenches and then to seek some possible countermeasures for minimizing the entry of water into the trenches. Also, investigation of transport of tritium to the atmosphere by plant root uptake of trench water and leaf transpiration is part of this study.

EXPERIMENTAL APPROACH

A transect across trench 19S and the adjacent area was instrumented as shown in Fig. 1. Two types of instrumentation were installed in the soil profile: (1) soil moisture cells (Soiltest Co.), and (2) mini-porous cups. The soil moisture cells were installed to allow measurements of relative soil moisture content (soil moisture tension gradients). The mini-porous cups were implanted very close (5 cm) to the soil moisture cells to allow extraction of soil water in the region of the soil moisture cells. Mini-porous cups were used instead of full-sized cups so as not to influence subsequent measurements made with the soil moisture cells. The mini-cups have a volume of approximately 2 ml and the soil solution samples are taken after the soil moisture cell readings. The soil moisture cells are then not read again until at least a two-week period has passed. The porous cups allow extraction of soil under unsaturated conditions down to about 70 centibars of soil water suction (tension); therefore, they can be used for sampling saturated or moist unsaturated soils. Electrical leads from each of the moisture sensors and fine tubing (bore-1 mm) from the mini-porous cups terminated in an instrument box mounted above the soil surface and to one side of the instrument stack or "station" located vertically in the soil profile.

Samples of Kentucky fescue grass were taken from plants grown on the caps of trenches 37, 38, and 39 and from nearby areas in a preliminary study of the possible transport of tritium by the fescue from the trenches to the atmosphere. The tritium present in the plant transpiration stream was determined by vacuum distillation of fresh grass samples and then liquid scintillation determination of the ^3H present in water collected. Since the grass samples were collected in the cold wet winter month of February, it was thought that the ^3H present in the transpiration stream at that time might be very low due to rainwater dilution. To look back in time, i.e. the previous fall when the grass was actively growing following a mowing, structural or organically bound ^3H was also determined. This was done by reacting the vacuum-dried plant material with oxygen at 900°C and then liquid scintillation of the water obtained from the reaction.

RESULTS AND DISCUSSION

Soil moisture cell measurements at two selected depths at station no. 1, and with the passage of time (February 1980 through September 1982), are given in Fig. 2. Station no. 1 was located approximately 9 m away from the edge of trench 19S and in an undisturbed area between trenches. The moisture sensor located at the 0.9 m depth indicated a rather strong seasonal cycling with an overdraft of water use by the Kentucky fescue crop during the late summer and fall and a replenishment of soil moisture at that depth during winter and spring by infiltration of water in excess of plant water use. At no time did the soil

become saturated at that depth. At the 2.4 m depth, there was little seasonal cycling, suggesting little plant root uptake of water from that depth in the soil profile or significant rainwater percolation to that depth. During the entire period, the soil at this depth remained unsaturated. Prior to October 1981, Kentucky fescue was grown on the site to control erosion and reduce intrusion of excess water into the trenches by plant water use as transpiration. In October of 1981 the fescue was removed and replaced with plastic sheeting on the soil surface with the goal of reducing water infiltration into the trenches. From Fig. 2 it is evident that the plastic sheeting was quite effective in preventing water entry into the soil profile at that location. At the 0.3 m depth, strong seasonal cycling was observed during the previous two years with the soil being substantially wet up during the winter and spring seasons. After application of the plastic, little change in moisture content was observed at the 0.9 m depth during the winter and spring of 1982. Application of the plastic membrane appeared to have little influence on the moisture content of the soil at the 2.4 m depth which is consistent with the conclusion previously reached that little plant root uptake from that depth was occurring or that there was significant rainwater percolation to that depth.

Fig. 3 depicts relative soil moisture at four depths in the trench cap on trench 19S with the passage of time (February 1980 through September 1982). At the 0.9 m depth, a very marked seasonal wetting and drying cycle was observed. During winter and spring, the trench cap was essentially saturated but was dried out substantially by plant extraction of water during the summer and fall periods. A similar moisture status was observed at the 1.5 m depth. At 2.4 m, little or no seasonal cycling was observed and the soil remained approximately saturated during the entire period of measurements. Application of a plastic membrane to the soil surface appears to be less successful in preventing water infiltration than it was at station 4. In July of 1982 repairs were made to the plastic membrane in the area of station 4 and it appears that the moisture content may be dropping, but passage of time with further measurements should be made before reaching such a conclusion.

From the observations given above concerning Figs. 2 and 3, it is evident that no water moved from station no. 1, located in the soil profile, to station no. 4, located in the trench cap, as to do so the water would have to move against a concentration gradient. Also Figs. 2 and 3 show that a plastic membrane, as a practical matter, can be an effective barrier to water infiltration but must be applied and maintained with great care.

In last year's Maxey Flats report, the ^3H concentrations in the soil solutions at stations no. 1 and no. 4 were given. It was found that the concentration of ^3H in the trench cap increased markedly with increasing depth, indicating the waste in the trench below the cap was the ^3H source and that ^3H was migrating upward into the cap by being carried in the upward movement of water during the summer and fall periods of water depletion by the fescue crop. At station no. 1,

9 m away from the trench, the ^3H was relatively low, and uniform with depth in the soil profile, indicating the evaporator was the source of the ^3H at this location, and not the waste in the trench located 9 m away. This condition would evidence no or little movement of water from the trench to the location of station no. 1. Also, in last year's report, results of a tracer experiment were given where an organic water tracer was used to follow rainwater infiltration into the trench cap of 19S. The data indicated that the rainwater infiltrated and percolated readily through the trench cap. All of the above information indicates that the trench caps are quite permeable to water and that percolation of rainwater through the trench caps is the major pathway of water entry into the trenches. The data indicate little substantial lateral water movement in the top few meters of the soil profile.

During the past year soil solution samples have been taken from greater depths in the soil profile, compared to previous years. Tritium concentrations in the soil solution at four dates are given in Table 1. This station was located 8 m away from Trench 19S. In last year's report it was shown that the ^3H concentration was quite uniform in the top 3.9 m of the soil profile in the area between trenches and it was concluded that the source of ^3H was the evaporator, not the trench. Table 1 furnishes further evidence of this, and in addition, the data shows how very slowly permeable to water the undisturbed soil profile is. After nine years of operation of the evaporator, only trace amounts of ^3H had reached the 7.6 m depth in the soil profile.

Data given in last year's report showed an increasing concentration of ^3H in the trench cap with depth. A question arises as to how the distribution of ^3H in the trench cap will be affected by the installation of the plastic membrane to the soil surface. Table 2 gives the ^3H concentration in the soil solution in the trench cap in 1980, in 1981 before application of the plastic membrane in the fall of 1981, and the distribution 10 months after the plastic was laid down. Little change seems to have occurred although this could have been influenced by leaks in the membrane. All apparent leaks were repaired in July of 1982 and the distribution of ^3H will be determined over the coming year.

Prior to the application of plastic to much of the Maxey Flats disposal site in the fall of 1981, Kentucky fescue was grown on the entire site. It is of interest to determine the magnitude of the transport of ^3H from the trenches to the atmosphere by plant root uptake and transpiration from the leaves.

In the winter of 1982, a preliminary study was made where grass samples were taken at various locations on the site, both over trenches without plastic and in undisturbed areas. It was found that it was necessary to get as removed as possible from the evaporator depositions of tritium to minimize confusion as to the source of the tritium in the plant transpiration stream, i.e. the evaporator or the trench water as the tritium source. Data in Table 3 gives the concentration of ^3H

in the leaf transpiration stream from fescue grown on the caps of trenches 37, 38, 39, and nearby areas. The ^3H in the transpiration stream was about seven times higher in the plants grown on the trench caps than that of the controls, but it was only about 1/1000 the concentration of the trench water. The concentration of the ^3H present as structural hydrogen in the organic material was about twice as high as it would be if it were in equilibrium with the transpiration stream. At equilibrium, the organic ^3H should be 60% of the $^3\text{H}_2\text{O}$ due to the ^3H concentration in $^3\text{H}_2\text{O}$ and $\text{C}^3\text{H}_2\text{O}$. The plant matter is mostly cellulose; therefore the $\text{CH}_2\text{O}/\text{H}_2\text{O}$ ratio is appropriate. The reason for the disequilibrium is probably that the plants were sampled in February 1982 during the wet, cold season and the H_2O tritium present in the plant would reflect rainwater dilution of the ^3H present in the soil. The organic tritium would have been "built in" during the growth period during the warmer, drier, growing period preceding the winter, thus furnishing a "look back" in time as to probable higher ^3H in the transpiration stream in the fall of 1981.

Since the tritium concentration in the soil solution will vary substantially with rainfall patterns, it was decided to set up a plot where year-round measurements of ^3H in the transpiration stream of fescue would be made. Such measurements would allow an estimate of annual transport of ^3H to the atmosphere by the fescue. The sampling pattern will be as shown in Fig. 4. Five 61 cm (2 ft.) diameter areas will be clipped and analyzed for ^3H in the grass. The boundaries of the trenches are not well known so a preliminary experiment has been carried out to insure locating the entire sampling location over a trench. Twelve locations were sampled in August 1982 per Fig. 4, hopefully over trenches 37, 38, or 39. Analyses of the ^3H in the leaves is not yet complete but the data available at this writing is given in Table 4. In addition to samples collected over trenches 37, 38, and 39, grass samples were also taken in the general area, but definitely away from the trenches. These samples will give the maximum ^3H contribution from the evaporator. Data from these samples are given in Table 5. It can be seen by comparing the data of Tables 4 and 5 that most of the ^3H present in the transpiration steam of the fescue growing over the trenches is due to plant uptake from the waste and not due to deposition from the evaporator. All the samples collected in the summer of 1982 including the "background" samples tend to be much higher in ^3H than the grass samples taken in the winter of 1982. When the analyses of the samples are completed, a plot will be selected for sampling throughout next year through a full seasonal cycle.

Close examination of the data given in Table 4 has led to the possibility that ^3H in the transpiration stream of the fescue might serve as an indicator of trench boundaries. Efforts to date, including a radar survey, to determine the trench boundaries have been less than successful. To get maximum sensitivity from this method the ideal sampling time would be in a drought period when the grass was obtaining the bulk of its moisture from deep in the trench caps. It is intended to pursue this idea during the coming year by taking grass transects across several trenches and determining the ^3H concentration in the plant water.

LYSIMETER EXPERIMENTS

The first goal of the project described here was to determine the principal pathway(s) of water entry into the waste burial trenches. The principal pathway has been determined to be percolation through the trench cap.

The second main goal is to study possible countermeasures for reducing the water entry into the waste burial trenches. At this time the Commonwealth of Kentucky is using a plastic membrane placed on the soil surface as a countermeasure. However, this must be considered a temporary countermeasure when the life of plastic is considered along with the half life of some of the buried radionuclides, such as plutonium-239 with its 24,000 year half life. An alternative to keeping the site covered with plastic for extremely long periods of time might be found in management techniques. It is felt that possible management techniques could best be studied using a simple lysimeter experiment. Accordingly lysimeters have been installed to enable prediction of site functions as affected by various types of site management, and possible procedures to be followed in site closing. Bulk density measurements were made on 19S and were found to be about 1.8 g/cm³; therefore the lysimeters were packed to that soil density. Soil fertility trials have been run at Berkeley and the soil has been found to be extremely deficient in phosphorus and nitrogen in addition to needing a lime application. The soil was not deficient in potassium or sulfur or any micronutrient. This information will be used in maximizing plant growth in the lysimeters with the goal of maximizing plant transpiration and minimizing water percolation to the water table. The lysimeters will allow complete water balance studies (Fig. 5); therefore the effects of crop types and management of the crops on increasing or decreasing water entry into waste burial trenches can be evaluated. The use of vegetative cover to reduce water percolation into waste burial trenches may lead to plant uptake and transport of radionuclides, especially ³H. To investigate this, lysimeter studies using trench water will be useful in quantifying radionuclide movement and especially ³H release to the atmosphere by evaporation of ³H₂O and plant transpiration of ³H₂O. The lysimeter ³H studies will be run in conjunction with detailed studies on the trench 37, 38, and 39 areas described earlier in this report.

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Soil depth, ft	1981	1982	1983	1984	1985
0.3	0.10×10^6	0.03×10^6	0.01×10^6	*	*
5.7	"	0.06	"	0.01×10^6	"
5.9	"	0.02	"	0.02	0.03×10^6
7.3	"	0.006	"	0.008	"

Table 1

^3H concentration in the soil solution at various depths in the soil profile at station 17A located 8 m away from trench 19S. Comparison with data given in Table 2, ^3H concentration in the trench cap, indicates that the evaporator was the source of the ^3H . In addition, the very low concentration of ^3H at the 7.6 m depth shows that the undisturbed profile is quite impermeable to percolating water.

Soil depth, m	^3H			
	2/81	5/81	9/81	8/82
	pCi/l			
0.3	0.10 $\times 10^6$	0.09 $\times 10^6$	*	*
2.7	0.06 "	0.04 "	0.09 $\times 10^6$	*
5.2	0.02 "	0.02 "	0.02 "	0.02 $\times 10^6$
7.6	0.006 "	0.008 "	0.007 "	0.004 "

*Soil too dry to obtain a soil solution sample.

Table 2

^3H concentration in soil solution of trench cap of trench 19S at station no. 4. There is a marked increase in ^3H with depth into the cap toward the waste indicating that the waste is the principal source of the ^3H and not the evaporator. Installation of the plastic membrane on the trench cap surface did not have a marked effect on the ^3H distribution in the trench cap.

Soil depth, m	^3H		plastic applied	8/82
	2/80	9/81		
	pCi/l			
0.15	0.28×10^6	--		0.59×10^6
0.30	0.65 "	0.57×10^6		0.43 "
1.50	1.07 "	0.97 "		0.43 "
2.10	2.07 "	1.85 "		0.86 "
2.40	7.93 "	5.23 "		3.70 "

Table 3

^3H concentration in leaves of Kentucky fescue grass grown on trench caps and nearby field (controls) at the southeast corner of the Maxey Flats site. Sampled February 1982. This was a preliminary study with one grass sample taken from each trench cap. The ^3H in the transpiration stream was about seven times higher in the plants grown in the trench caps than in that of the controls, but it was only 1/1000 of the trench water. The organic (structural) ^3H was twice as high as it should have been at equilibrium with the ^3H present in the transpiration stream indicating probable higher ^3H concentration in the soil solution and transpiration stream during the growing season of the past fall.

Trench number	^3H concentration in plant sap [†] ($^3\text{H}_2\text{O}$)	^3H concentration in trench water ($^3\text{H}_2\text{O}$)	^3H concentration in leaf organic material [‡] ($\text{C}^3\text{H}_2\text{O}$)
	pCi/l		
37	6.9×10^4	3.7×10^7	9.7×10^4
38	3.5 "	3.3 "	4.3 "
39	10.5 "	10.1 "	14.0 "
Control	1.1 "	---	2.0 "
Control	1.0 "	---	2.0 "
Control	0.9 "	---	1.0 "

[†]Determined by vacuum distillation of fresh leaf material then liquid scintillation of the $^3\text{H}_2\text{O}$ distilled off.

[‡]Determined by reacting vacuum-dried leaf material with O_2 at 900°C , then liquid scintillation of the resulting $^3\text{H}_2\text{O}$.

Table 4

Tritium in transpiration stream of fescue grass. Purpose of sampling was to locate a uniform area to use for repeated sampling to determine the annual transport of ^3H to the atmosphere by the transpiration stream of fescue. Location of trench boundaries are not well known and evidently some samples were not taken from over a trench. This observation suggests that ^3H concentration in the transpiration stream may serve as an accurate indicator of the location of trench boundaries.

Sample No.	Trench No.	^3H , pCi/l	Sample No.	Trench No.	^3H , pCi/l
1N	38	0.12×10^6	7N	39	1.18×10^6
1E	"	0.14 "	7E	"	0.91 "
1S	"	0.43 "	7S	"	6.97 "
1W	"	**	7W	"	108.76 "
1C	"	0.44 "	7C	"	3.79 "
2N	38	0.13 "	8N	38	0.84 "
2E	"	0.65 "	8E	"	0.71 "
2S	"	**	8S	"	1.05 "
2W	"	**	8W	"	2.09 "
2C	"	0.40 "	8C	"	1.05 "
3N	38	0.12 "	9N	37	0.25 "
3E	"	**	9E	"	0.27 "
3S	"	**	9S	"	0.24 "
3W	"	**	9W	"	0.28 "
3C	"	0.36 "	9C	"	0.27 "
4	38	0.27 "	10N	37	0.67 "
4	"	0.50 "	10E	"	1.07 "
4	"	0.30 "	10S	"	1.31 "
4	"	0.26 "	10W	"	0.18 "
4	"	0.27 "	10C	"	0.63 "
5	38	1.63 "	11N	37	0.44 "
5	"	**	11E	"	0.67 "
5	"	**	11S	"	0.37 "
5	"	**	11W	"	0.07 "
5	"	0.29 "	11C	"	0.46 "
6	39	0.30 "	12	38	0.12 "
6	"	**	12	"	0.12 "
6	"	**	12	"	0.18 "
6	"	**	12	"	0.13 "
6	"	0.43 "	12	"	0.14 "

**Samples collected but not yet analyzed.

Table 5

Tritium concentrations in transpiration stream of fescue grass taken in general area of trenches 37, 38, and 39 but sufficiently removed from trenches so roots will not reach waste. Tritium in the transpiration streams will be an indicator of maximum contribution of ^3H from evaporator.

Sample No.	Location	^3H pCi/l
13N	South fence line	0.09×10^6
13E	"	0.09 "
13S	"	0.31 "
13W	"	0.08 "
13C	"	0.11 "
14N	West fence line	0.13 "
14E	"	**
14S	"	**
14W	"	**
14C	"	0.10 "
15N	Open field, SE on site	0.11 "
15E	"	0.11 "
15S	"	**
15W	"	**
15C	"	0.09 "
16N	Open field, SE on site	0.11 "
16E	"	0.11 "
16S	"	**
16W	"	**
16C	"	**

**Samples collected but not yet analyzed.

Figure 1 - Profile view of instrumental transect across trench 19S and adjacent soil. The exact location of the trench wall is not known but is known within approximately ± 1 m, or closer, from borings.

Figure 2 - Relative soil moisture content at 2 depths in soil profile, station no. 1, 9 m away from trench 19S, during the period February 1980 through September 1982. Strong seasonal cycling is shown at the 0.9 m depth and little seasonal cycling at the 2.4 m depth. Soil profile remained unsaturated at all times. A plastic membrane on the soil surface was installed in the fall of 1981 and was effective in preventing infiltration of water into the soil profile during the winter and spring of 1982.

Figure 3 - Relative soil moisture contents at 4 depths in a trench cap of trench 19S, during the period February 1980 through September 1982. A marked seasonal cycling was observed at the 0.9 m depth and the soil was essentially saturated in the winter and spring at that depth. It was substantially dried out during the summer and fall by overdraft water extraction by the Kentucky fescue. A similar moisture pattern was observed at the 1.5 m depth. At 2.4 m into the trench cap, little or no seasonal cycling was observed and the soil remained approximately saturated during the entire period of measurements. A plastic membrane was installed on the soil surface in the fall of 1981. Leakage of water past the membrane during the winter and spring of 1982 is evident, repairs were made to the membrane in July of 1982.

Figure 4 - Diagram of fescue sampling procedure. Each sampling location consists of 5 circles each 61 cm (2 ft) in diameter inside of a 244 cm (8 ft) diameter circle and 15 to 20 g of grass clipped from each 61 cm circle. Twelve such locations were sampled on trenches 37, 38, and 39 in August 1982. The location of trench boundaries is not known with accuracy and this procedure should allow selection of an area for sampling located entirely over a trench and with reasonably uniform ^3H concentration in the transpiration stream of the Kentucky fescue. Upon selection of a sampling location, ^3H will be measured in the transpiration stream on a monthly basis in each of the five circles. Measurement for a full year throughout the four seasons should give a measure of the annual transport of ^3H to the atmosphere by the fescue grass.

Figure 5 - Cross section of an installed lysimeter. System gives complete accountability of all rain water falling on soil surface. Amount of water striking soil surface is known from rainfall measurements. Over a sufficiently long time period, the water striking the surface has three fates: I. Surface run-off. Measured by collection in surface run-off sump and pumping to collection tank. II. Deep percolation to the water table. Measured by maintaining constant water table level by pumping to storage tank. III. Surface evaporation and plant transpiration. Surface evaporation and plant transpiration = rainfall - (surface run-off + deep percolation). Lysimeters to be used to evaluate effects of crop type, management, and also radionuclide migration studies, especially transport of ^3H from water table to the atmosphere by plant uptake and transpiration.

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14. ABSTRACT (200 words or less)

Subsurface waters at Maxey Flats are anoxic, have a high alkalinity and contain high concentrations of ferrous, sulfide and ammonium ions and organic carbon. The trench leachates are extremely variable in composition. Prominent radionuclides include ^3H , ^{60}Co , ^{90}Sr , ^{137}Cs , $^{238,239,240}\text{Pu}$ and ^{241}Am . A wide spectrum of dissolved organic compounds is present in the leachates, including EDTA, polar organics and decomposition products from the waste forms. Cobalt-60 and plutonium are present as EDTA complexes and ^{90}Sr and ^{137}Cs are associated with carboxylic acid type compounds. The chemistry of these waters changes drastically as they become oxic and plutonium becomes less mobile under these new conditions. Water enters the trenches by infiltration through the trench caps, through subsidence areas, and through interfaces between new landfill and the original soil. Lateral flow is very complex and slow, and apparently occurs mainly by fracture flow. The plastic infiltration barrier installed in 1981-1982 has been effective in reducing soil moisture if cracks and leaks are eliminated. To date, no direct evidence of radionuclide transport to offsite locations by subsurface flow has been confirmed. The offsite distribution of radionuclides, except for tritium, is comparable to the ambient fallout from nuclear weapons testing. Tritium concentrations in water off-site are orders of magnitude below MPC levels.

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