

MASTER



INTERNATIONAL SYMPOSIUM
ON MIGRATION IN THE TERRESTRIAL ENVIRONMENT OF
LONG-LIVED RADIONUCLIDES FROM THE NUCLEAR FUEL CYCLE

Knoxville, Tennessee, USA, 27-31 July 1981

PNL-SA--9122
CONF

IAEA-SM-257/ 55P

CONF-810722--9

CHEMICAL SPECIES OF MIGRATING
RADIONUCLIDES AT A SHALLOW LAND LOW-LEVEL
RADIOACTIVE WASTE BURIAL SITE

L. J. Kirby
A. P. Toste
C. L. Wilkerson

Physical Sciences Department

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

PACIFIC NORTHWEST LABORATORY
Operated by Battelle for the
U.S. Department of Energy
Under Contract DE-AC06-76RLO 1830
Richland, Washington, U.S.A. 99352

This is a preprint of a paper intended for presentation at a scientific meeting. Because of the provisional nature of its content and since changes of substance or detail may have to be made before publication, the preprint is made available on the understanding that it will not be cited in the literature or in any way be reproduced in its present form. The views expressed and the statements made remain the responsibility of the named author(s); the views do not necessarily reflect those of the government of the designating Member State(s) or of the designating organization(s). In particular, neither the IAEA nor any other organization or body sponsoring this meeting can be held responsible for any material reproduced in this preprint.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

CHEMICAL SPECIES OF MIGRATING
RADIONUCLIDES AT A SHALLOW LAND LOW-LEVEL
RADIOACTIVE WASTE BURIAL SITE

L. J. Kirby
A. P. Toste
C. L. Wilkerson

ABSTRACT

A research program at the Maxey Flats, Kentucky (U.S.A.) waste disposal site has been undertaken to define the chemical species contributing to the migration or retention of radionuclides contained in waste buried at that site. An experimental trench and inert atmosphere sampling wells were installed to sample water for determination of the chemical species of migrating radionuclides. The organic ligands are studied by gas chromatography, steric exclusion chromatography and mass spectrometry; and the data correlated with specific radionuclide counting data to determine precise chemical species. Preliminary data are reported in the text.

INTRODUCTION

The Maxey Flats radioactive waste burial site, opened for burial in 1963, was closed in 1977 due to difficulties which included seepage of water from the burial trenches. This area normally receives relatively high rainfall, and considerably greater problems have been experienced than are observed at burial sites in arid regions of the country. At Maxey Flats, interpretation is complicated because radioactivity could have spread by sources other than subsurface transport. Burial trench caps have subsided and reworking to form new caps has resulted in some general low-level contamination. Other known sources of contamination include atmospheric transport from the evaporator plume and spillage of radioactive liquids. Consequently, it is very difficult from currently available information to distinguish between environmental contamination from these sources and radionuclide migration by subsurface aquifer transport.

Subsurface migration of radionuclides depends on their chemical forms, and chemical form is thus one of the most serious considerations associated with long-term isolation of radioactive wastes. For example, hexavalent plutonium and uranium migrate through soil faster than their corresponding tetravalent species, and technetium migrates faster as pertechnetate ion than it does in the reduced form. Decontaminating agents buried with radioactive wastes provide complexing ligands for radionuclides that may enhance their ability to migrate. Furthermore, radionuclide complexes may be formed following bacterial degradation of organic materials and concurrent oxidation-reduction processes to form mobile radionuclide species. All of these factors must be considered in interpreting analytical data from Maxey Flats.

OBJECTIVES

The objectives of this research program are to determine the amounts and chemical species of radionuclides which are moved by subsurface routes; to determine the chemical species of radionuclides in waste burial trenches and compare these with the species observed in monitoring trenches and wells, springs or seeps and surface flow from the site; and to determine the surface distribution of radionuclides over the waste burial site and adjacent areas. A fourth objective emphasizes the need to coordinate implementation of the above objectives with the implementation of the objectives of closely related research programs at the Maxey Flats waste burial site.

METHODS

Field Studies

Because of the small amount of definitive information on radionuclide movement at Maxey Flats, a program to define subsurface movement of radionuclides has been given a very high priority. The initial method chose to study radionuclide movement was to construct an experimental slit trench adjacent to one of the existing waste burial trenches. The trench was designed to accommodate a variety of research efforts. Sumps were installed to study saturated flow. Porous cups and soil moisture cells were installed in the trench wall, cap and adjacent area to study unsaturated flow near the trench. Nonradioactive tracer studies were included to monitor tracer movement from the experimental trench and to study the permeability of the trench caps to water movement and to root penetration. Several varieties of vegetation were planted to study the agricultural aspects of trench capping. Engineering studies of trench capping and surface drainage were included because of the importance of erosion and rainwater penetration into the trenches.

In a second and related construction effort, 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 in an inert 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 subsurface water.

Laboratory Studies

Tritium analyses were performed by liquid scintillation spectrometry and ^{90}Sr was chemically separated and counted using a beta proportional counter. Gamma-emitting radionuclides were analyzed by

gamma-ray spectrometry using a Ge(Li) detector. Plutonium and americium were determined using solid state detectors and alpha energy analysis.

Organic analyses were performed following steric exclusion chromatography. The water sample was first concentrated by rotary evaporation and the pH adjusted to that of the original sample. 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 UV absorbance at 254 nm and collected using a fraction collector. Each column fraction was acidified with HCl and divided into equal portions to be used for destructive radionuclide analysis and nondestructive analysis for gamma-emitting radionuclides and organic compounds.

The subfraction 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). The aqueous fraction believed to contain water-soluble, polar organic compounds was evaporated to dryness under nitrogen. The residue of each fraction was then methylated with BF_3 /methanol and incubated 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 was then evaporated under nitrogen, the residue redissolved in chloroform and an aliquot analyzed by GC and by mass spectrometry (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 quantitate the various organic constituents in the GC samples. MS analyses were performed on a ZAB high resolution mass spectrometer by direct-probe inlet mass spectrometry at a resolution of approximately 4000. Electron impact ionization (70 eV) was used. The ion source was maintained at a nominal 100°C .

RESULTS AND CONCLUSIONS

Radionuclides in Subsurface Water

Water flowed into three sections of the experimental trench during construction and samples were taken for radionuclide analysis. The radionuclide concentrations were comparable to trench leachate from the adjacent waste trench for ^3H and ^{90}Sr , and somewhat lower for the other radionuclides. On several subsequent sampling trips to Maxey Flats, water was collected from the experimental trench sumps for radionuclide analysis. Radionuclide concentrations in the latter samples were significantly lower, and only ^3H remained at levels comparable to the concentrations in the samples taken during construction.

The radionuclide concentrations in samples taken during trench construction clearly show that subsurface movement of radionuclides has occurred at Maxey Flats. The marked decrease in most radionuclide concentrations observed on resampling the experimental trench indicated that the trench design had adversely influenced the concentration of radionuclides in water flowing toward the trench sumps. Column experiments with the crushed rock used to backfill the trench showed that the rock alone had negligible effect in the absence of oxygen. These experiments indicated that the exposure of the open trench to air during construction resulted in the formation of an in-place scavenger (ferric hydroxide), which reacts synergistically with the crushed rock to form an absorptive barrier for radionuclide transport.

Having established the need for sampling stations in undisturbed ground near the experimental trench, several inert atmosphere sampling wells were installed. Water samples collected from these wells were highly variable from well to well and support the view that subsurface flow at Maxey Flats is highly dependent upon fractures in the weathered shale and/or sandstone marker bed.^[1] In two locations samples from adjacent wells drilled a few meters apart differed in radionuclide content by several orders of magnitude, and indicated that at least two of the wells were very closely related to waste sources and possibly connected to them by fractures.

Chemical Species of Radionuclides

The initial determinations of the chemical species of radionuclides in water from the experimental trench were inconclusive because aging of the samples had taken place before they could be analyzed in the laboratory. Americium-241, ¹³⁷Cs, and ⁹⁰Sr were present in cationic species at the time of analysis, and only a small fraction of the total ⁶⁰Co present was anionic. Plutonium radionuclides were present in cationic, anionic, and nonionic forms. Physical changes had taken place in the samples (e.g., the tendency to form ferric hydroxide) and these changes probably altered the original ionic species.

The first measurements underscored the need to make such separations within the undisturbed water if possible. Apparatus was prepared to permit ion exchange separations and solvent extraction separations to be conducted anoxically at the source of the water. Americium-241 and ¹³⁷Cs were below detection levels in these sump solutions because the low concentrations and limited resin bed size precluded the collection of sufficiently large samples. Cobalt-60 was present in anionic species, and plutonium was present primarily as anionic species, although some cationic species were present or were produced by competition between the plutonium complex and the cation resin.

Solvent extractions were performed concurrently with the ion exchange experiments. None of the plutonium which passed through the anion resin column was extractable with thenoyltrifluoroacetone (TTA) in xylene. About 25% of the plutonium in the effluent from the cation resin column could be extracted, indicating that the TTA could compete favorably for some of the complexed plutonium. The results of the solvent extraction and ion exchange experiments indicate that the plutonium complex in the sump water is present primarily as an anionic species and exists in trivalent and tetravalent forms.

On the basis of GC and MS analyses, the chelating agent EDTA was identified as the major organic component in Maxey Flats sump water from Trench 27 but other polar, water-soluble organics were also present (Figure 1). The EDTA concentration was calculated to be $2.85 \times 10^{-6} \mu\text{M}$ (0.99 ppm). NTA and DTPA, other chelating agents like EDTA, were not detected in the sample. After steric exclusion chromatography with Sephadex G-15, several UV-absorbing peaks appeared, corresponding to column-included, organic-containing species (Figure 2). Plutonium eluted in one region of the UV chromatogram, just prior to ^{90}Sr and ^{137}Cs (Figure 2). EDTA co-eluted with plutonium, suggesting that EDTA is complexed with plutonium in the sump water. Preliminary results indicate that a variety of organic acids and other water-soluble, polar compounds co-eluted with the ^{90}Sr and ^{137}Cs . It thus appears that chelation of radionuclides by polar organic species such as organic acids may provide a mechanism for the migration of radionuclides at the waste burial site.

ACKNOWLEDGEMENTS

We are indebted to the Commonwealth of Kentucky for their cooperation in this research. Particular thanks go to Mr. John Razor and his co-workers at Maxey Flats for their assistance and encouragement. This work was performed for the U. S. Nuclear Regulatory Commission under Contract DE-AC06-76-RLO 1830.

REFERENCES

- [1] H. H. Zehner, "Preliminary Hydrogeologic Investigation of the Maxey Flats Radioactive Waste Burial Site, Fleming County, Kentucky," U.S. Geological Survey Open File Report 79-1329 (1979).

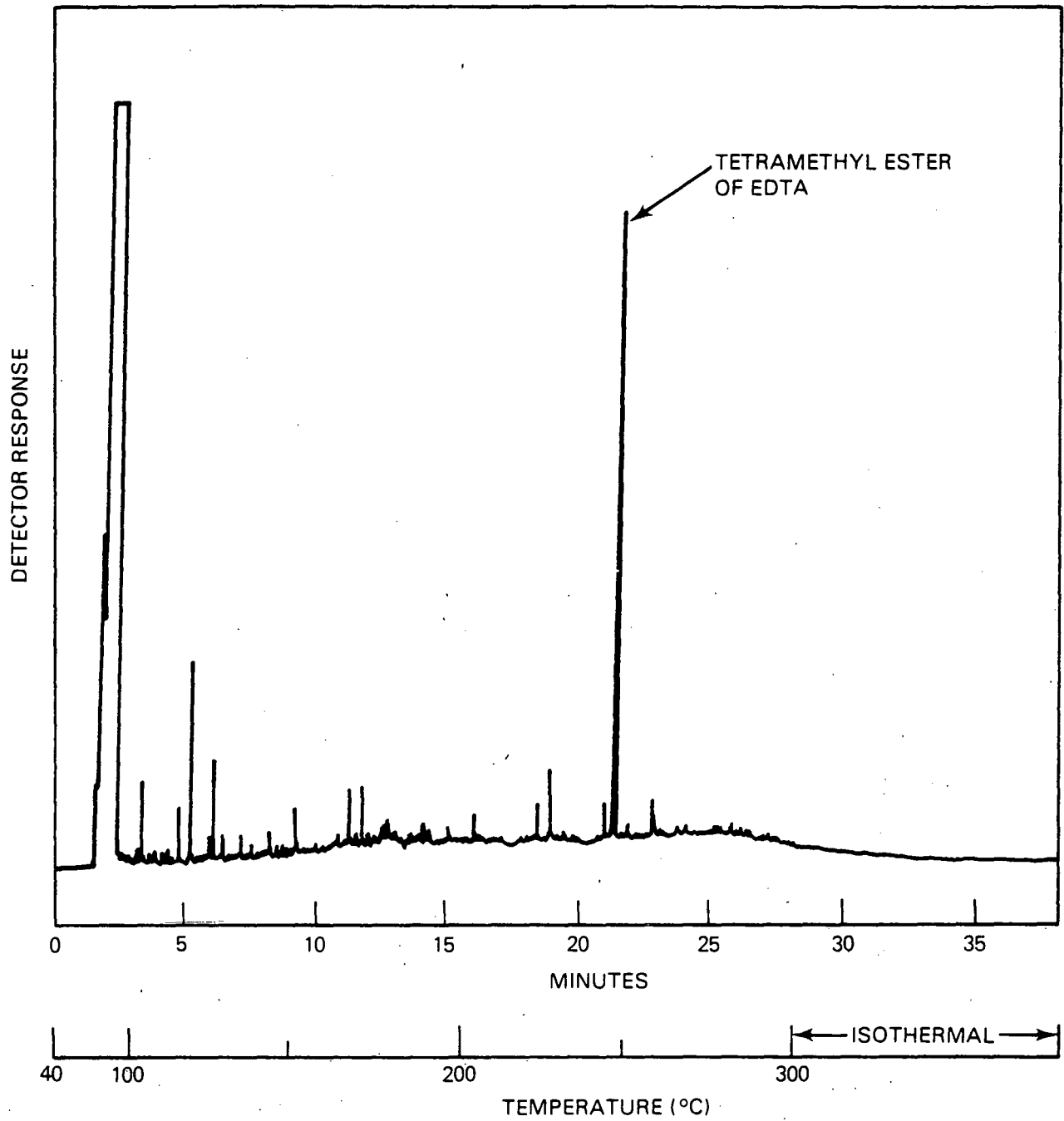


FIGURE 1. GC Chromatogram of Methylated Aqueous Fraction of Maxey Flats Sump Water from Waste Trench 27 (10-Fold Concentrate)

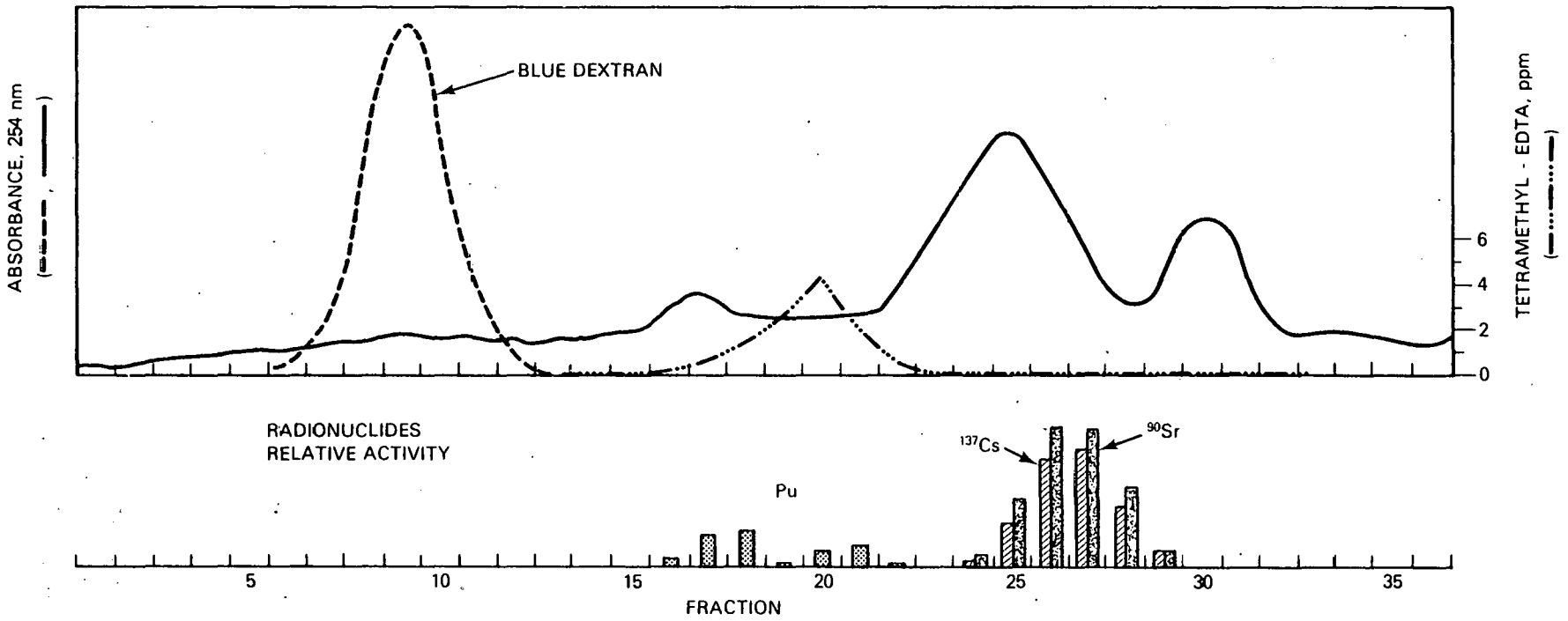


FIGURE 2. Steric Exclusion Chromatography (Sephadex G-15) Fractionation of Maxey Flats Sump Water from Waste Trench 27 (10-Fold Concentrate)

LIST OF FIGURES

<u>Figure No.</u>		<u>Page No.</u>
1	GC Chromatogram of Methylated Aqueous Fraction of Maxey Flats Sump Water from Waste Trench 27 (10-Fold Concentrate)	7
2	Steric Exclusion Chromatography (Sephadex G-15) Fractionation of Maxey Flats Sump Water from Waste Trench 27 (10-Fold Concentrate)	8