

ORGANIC GEOCHEMICAL STUDIES
AT A COMMERCIAL SHALLOW-LAND DISPOSAL SITE
OF LOW-LEVEL NUCLEAR WASTE

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ABSTRACT

The subsurface migration of radionuclides has been studied at a commercial, shallow-land burial site of low-level nuclear waste at Maxey Flats, Kentucky. A variety of radionuclides including ^3H , $^{238+239+240}\text{Pu}$, ^{60}Co , ^{137}Cs and ^{90}Sr have migrated short distances on-site (meters to tens of meters). A number of the mobile radionuclides, notably plutonium and ^{60}Co , appear to exist as anionic species with organic properties. As a result, we have studied the organic geochemistry of radioactive leachates pumped from a number of waste burial trenches throughout the site. The major aim of the organic research is to elucidate the role of organic compounds in mediating the subsurface migration of the mobile radionuclides in groundwater. A survey study of the hydrophilic and hydrophobic organic content of the waste leachates has revealed that organic compounds are readily leached from the buried waste. Organic chelating agents like EDTA, HEDTA and ED3A are the major hydrophilic organic compounds in the leachates, their concentrations ranging from 78 ppb to 19,511 ppb. A number of carboxylic acids are also present in the leachates, ranging from 671 ppb to 8,757 ppb, collectively. A variety of hydrophobic organic compounds including barbiturates and other aromatic compounds, presumably waste-derived, are also present in the leachates, generally at lower ppb concentrations. A detailed chemical speciation study, aimed at determining whether any of the organic compounds identified in the survey study are associated with the mobile radionuclides, was undertaken using leachate from one of the waste trenches. It is clear that EDTA is chelated to plutonium and ^{60}Co in the leachate, potentially mobilizing these radionuclides. Other radionuclides, ^{137}Cs and ^{90}Sr , may be associated with polar organic compounds such as carboxylic acids.

INTRODUCTION

Shallow-land burial continues to be the preferred method of long-term disposal of low-level nuclear waste in the United States. Commercial shallow-land burial of low-level waste has existed in the U.S. for over two decades at six sites: Maxey Flats, Kentucky; West Valley, New York; Barnwell, South Carolina; Sheffield, Illinois; Beatty, Nevada; and Hanford, Washington. In spite of this, much still remains to be understood about the subsurface migration of radionuclides in groundwater. Perhaps one of the least understood areas is the role of organic compounds in mediating the migration of radionuclides in groundwater. For example, does the organic content of soil particles enhance the retardation of radionuclides? On the other hand, do organic chelating agents, natural (bio-organic) or synthetic (waste-derived), facilitate the migration of certain radionuclides in groundwater?

The major aim of this report is to familiarize radwaste researchers with the importance of organic research in nuclear research. The organic chelating agents are of obvious concern. Are organic chelating agents in decontamination wastes leachable by groundwater, and to what extent are they chelated to the waste's radionuclides? In addition to chelating agents, however, the organic content of low-level nuclear waste may include non-radioactive but toxic compounds which are environmentally unacceptable. Which waste-derived organic compounds are leached by groundwater? What information can their analysis provide about the subsurface migration of radionuclides?

Researchers at Pacific Northwest Laboratory (PNL) are currently studying the subsurface migration of radionuclides at several shallow-land burial sites in the U.S. and Canada. In the past few years, we have expanded our geochemical studies of radionuclide transport to include organic geochemical studies. This expansion of effort has been most evident in our research at the Maxey Flats burial site in Kentucky. Using this site as a model system, we have studied the geochemistry of organic chelating agents and other waste-derived organic compounds, including their diagenesis, in an effort to assess the role of radionuclides.

In this report we describe two research efforts on organic geochemistry at Maxey Flats. First, we have completed a survey study of the organic content of waste leachates from waste trenches throughout the site. Second, we have begun a detailed chemical speciation study to determine which organic compounds identified in the survey study are complexed or chelated to radionuclides.

BACKGROUND

Maxey Flats is a plateau in northeastern Kentucky approximately 19 km from the city of Morehead. The nuclear waste burial site occupies approximately 0.08 km² of the plateau and sits approximately 90-122 m above the surrounding valleys¹. The lithology of the site consists of thick layers of fractured shale, which is relatively impermeable to groundwater flow, separated by thinner layers of sandstone. Waste has been buried in slit trenches excavated down to the first sandstone layer. Trench dimensions range up to

approximately 100 m in length, up to approximately 16 m in width, and up to 6 m in depth.

Waste burial at Maxey Flats began in 1963. Over the next 14 years, approximately 2.4 million curies of by-product material, plus 432 kg of special nuclear material (including 64 kg of plutonium) and over 242,000 kg of source material were buried at the site. A number of problems finally forced the site to close in 1977. Trace amounts of waste radionuclides were detected in the surrounding environs. A number of serious water management problems plagued the site. Decomposition of waste containers followed by compaction of the waste led to subsidence of the soil trench caps. The resulting holes were quickly filled and the trench caps mounded with soil to promote the runoff of rainwater. Despite such remedial construction efforts, however, rainwater entered the breached burial trenches and accumulated because of the soil's impermeability, leaching radioactivity from the buried waste. The excessive accumulation of radioactive leachate forced the site's operators to dewater the trenches by pumping the leachate and concentrating it in an evaporator. The evaporation operation, in turn, resulted in atmospheric transport of low levels of certain radionuclides in the evaporator plume, primarily tritium. In the past two years the site has been covered with a temporary geomembrane (plastic cover) to minimize infiltration by rainwater. This effort has proven successful enough to permit the evaporator to be shut down temporarily.

The factors governing subsurface migration of radionuclides at the Maxey Flats site appear to be extremely complex. Previous research conducted at the Maxey Flats site clearly indicates that the mobility of radionuclides in groundwater depends on their physicochemical form³⁻⁸. Plutonium was detected in waste leachate and appeared to be chelated to the chelating agent EDTA^{3,4,5-8}. Subsequent research at PNL has confirmed these earlier observations by researchers at PNL and other laboratories and provided new insights on the subsurface migration of radionuclides. The most abundant radionuclides in waste leachates from Maxey Flats are ³H, ⁶⁰Co, ⁹⁰Sr, ¹³⁷Cs, ²³⁸Pu, ^{239,240}Pu, and ²⁴¹Am⁹. Unlike the other radionuclides, the mobile forms of ⁶⁰Co and ²³⁸Pu proved to exist mainly as soluble anionic species¹⁰. Moreover, the mobile, anionic plutonium proved to be mainly Pu⁴⁺, with some Pu³⁺ also present. This was initially surprising because Pu⁴⁺ and Pu³⁺ are typically quite immobile in soil solutions¹¹. The high organic carbon content of Maxey Flats leachates (e.g., 160-1500 ppm) suggested that organic complexation might account for the mobility of the Pu, as well as the ⁶⁰Co, in the groundwater⁹. At this point, we expanded the scope of our chemical speciation research at Maxey Flats to include organic research.

EXPERIMENTAL

Sample Collection

Eight aqueous waste leachates were collected from six waste trenches scattered throughout the Maxey Flats disposal site (Fig. 1). Seven of the samples were pumped from trench sumps by researchers from Brookhaven National Laboratory (BNL) in October 1979 (waste trench 27) and October 1981 [waste trenches 7 (sump 3), 19 (sump W), 23 (sump M), 33 (sumps L-4 and L-8), and 35] and analyzed for organic compounds in our laboratory at PNL as part of a cooperative research effort. Researchers at BNL characterized the inorganic and radionuclide content of these leachates. The samples were stored at 4°C and in an

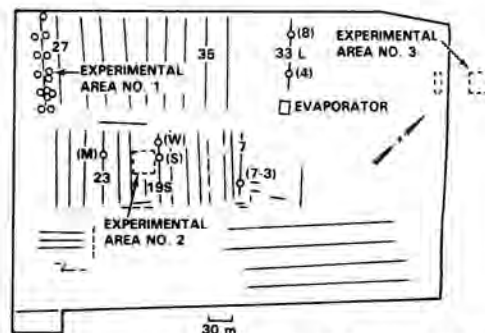


Figure 1. Commercial Shallow-Land Burial Site of Low-Level Nuclear Waste at Maxey Flats, Kentucky.

inert atmosphere at BNL's laboratory to prevent oxidation. Because these samples were originally collected for inorganic analyses, each of the samples was filtered with a 0.45 μ m filter and preserved by acidification with ultrapure nitric acid prior to analysis. After shipment to PNL, the acidified samples were stored at 4°C in Teflon bottles prior to sample preparation. Two additional leachates were collected by researchers from PNL in October 1979 (waste trench 27) and in July 1982 [waste trench 19S (sump S)]. These samples were pumped from the trench sumps using peristaltic pumps and collected under argon in Teflon or glass bottles. They were degassed with argon and sealed tightly for shipment to the laboratory, where they were stored in a refrigerated room at approximately 4°C prior to sample preparation.

Radiochemical Analysis

For the purposes of this report, radionuclide analyses were done at PNL for the detailed speciation study (steric exclusion fractionation) on the leachate from waste trench 19S. A number of procedures were used to analyze the radionuclide content of the groundwater samples. Tritium analyses were performed by liquid scintillation spectrometry; ⁹⁰Sr was chemically separated and counted on 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 following radiochemical separations. Nonradioactive species were analyzed by neutron activation analysis using a subcritical neutron multiplier¹², and by chemical and instrumental analysis.

Organic Analyses

Sample Preparation. Organic analyses were performed on whole water samples, i.e., no chromatographic fractionation, (survey study) and on a fractionated water sample, following steric exclusion chromatography (detailed speciation study). For the survey study, 50 mL of each water sample was concentrated to near dryness by rotary evaporation prior to organic derivatization. Leachate from waste trench 19S was selected for the detailed speciation study; 440 mL of the water was concentrated to 20 mL and the pH adjusted to that of the original sample (pH 7.6). Each solution was filtered, loaded on a Sephadex G-15 column, and chromatographed with Milli Q-purified water at a flow rate of 34 ml/hr. 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 divided into two portions, one for radionuclide analysis and the other for organic analysis.

Each concentrated survey sample and column fraction was extracted with chloroform to remove hydrophobic organic compounds; this extract, the hydrophobic organic fraction, was concentrated and set aside for analysis by gas chromatography (GC) and combined GC-mass spectrometry (GC-MS). The extracted water sample, containing hydrophilic organic compounds, was evaporated to dryness under nitrogen. The residue of each aqueous fraction was then methylated in a sealed reaction vial with 1 ml of BF_3 /methanol (14% w/v) at 100°C for 40 min. After cooling, 1 ml of chloroform was added, the mixture was transferred to a test tube containing 3 ml of 1M KH_2PO_4 buffer solution (pH 7) with a 0.2 ml chloroform rinse and vortexed. Part of the chloroform layer (0.6 ml), which contained the methylated hydrophilic organic compounds, was then evaporated under nitrogen. The residue was redissolved in chloroform and analyzed by GC and GC-MS.

GC Analysis. GC analyses were performed on a Hewlett-Packard 5880 gas chromatograph equipped with a 60 m x 0.25 mm I.D. fused silica capillary column coated with a 0.25 μm film of SE-52 and a splitless injection system. From an initial value of 40°C, the column temperature was programmed at 20°C per minute for 3 minutes to 100°C followed by 8°C per minute for 25 minutes to 300°C, and finally maintained isothermally at 300°C for 10 minutes.

GC-MS Analysis. 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 a 0.25 μm of SE-54; the column was programmed from 40°C to 300°C at 5°C per minute, where it was maintained isothermally for 8 minutes. A splitless injection system was used to introduce the sample onto the GC-MS instrument. A mass range of 50 to 400 amu was scanned every 1.0 sec by computer (HP-7920 Large Disc Drive).

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

Materials

Standards. The standards used in the GC analyses were purchased from Aldrich Chemical Company (Milwaukee, Wisconsin), United States Pharmacopoeial Convention, Inc. (Rockville, Maryland) and Sigma Chemical Company (St. Louis, Missouri).

Chromatographic Columns. The glass columns (2.5 cm x 45 cm) and the Sephadex G-15 used in the detailed speciation study were purchased from Pharmacia Fine Chemicals (Piscataway, New Jersey). The SE-52 and SE-54 silica capillary columns used in the GC and GC-MS studies were purchased from J&W Scientific, Inc. (Rancho Cordova, California).

Reagents, Solvents and Glassware. The BF_3 /Methanol (14% w/v) used in the methylation reaction was purchased from Regis Chemical Company (Morton Grove, Illinois). All of the solvents used in the organic

analyses were redistilled-in-glass solvents purchased from Burdick and Jackson Laboratories, Inc. Deionized water, prepurified for laboratory use, was further purified on a Milli-Q system (Millipore) containing two ion exchange resins and two charcoal filters. All glassware was acid cleaned in a hot solution of sulfuric acid/nitric acid (4:1 v/v).

RESULTS AND DISCUSSION

The analytical procedures developed for the organic analysis of the waste leachates from Maxey Flats have yielded considerable information about the leachates' hydrophilic organic fraction, where organic ligands of radionuclides like synthetic chelating agents reside. Work-up of the hydrophilic organic fraction yielded another fraction, the hydrophobic organic fraction. Its analysis, we contend, also yields important environmental information, some of which may touch on the subsurface migration of radionuclides. Finally, the detailed chemical speciation procedure using steric exclusion chromatography has yielded some important information about the association of hydrophilic organic compounds with radionuclides.

Hydrophilic Organic Compounds

Quite a variety of hydrophilic organic compounds were identified in the waste leachates (Table I). Six classes of compounds are represented: synthetic chelating agents containing ethylenediamine as a core; dicarboxylic acids; monocarboxylic acids; oxygenated carboxylic acids; aromatic carboxylic acids; and phthalic acid esters. The chelating agents are typically used in decontamination operations at nuclear facilities. The four classes of carboxylic acids are common biorganic compounds or their microbial diagenesis products. Phthalates are used heavily in industry as plasticizers in plastics and may also be microbial diagenesis products.

The most abundant class of hydrophilic organic compounds identified in the waste leachates are the chelating agents, ranging from 22.9 ppm in trench 19W down to 0.08 ppm in waste trench 33L-8. Three chelating agents were identified in the leachates: ethylenediaminetetraacetic acid (EDTA), N-hydroxyethylethylenediaminetriacetic acid (HEDTA), and ethylenediaminetriacetic acid (ED3A). EDTA is common to all of the leachates over a wide range of concentrations, ranging from 12.4 ppm in trench 19W down to 0.08 ppm in trench 33L-8. EDTA is the most abundant chelating agent in the leachates, with the exception of trench 23M where HEDTA is most abundant. The relative abundance of EDTA in the leachates varies considerably: it constitutes 81% of the chelating agent pool in trench 7-3; 54% in trench 19W; 71% in trench 19S; a low 17.3% in trench 23M; 82% in trench 27; and 100% in trenches 33L-4, 33L-8 and 35. These differences undoubtedly reflect differences in the wastes originally buried, as well as differences in the microbial and/or chemical environments of the waste trenches.

Overall, HEDTA is the second most abundant chelating agent in the waste trenches. In trench 23M it is the most abundant hydrophilic organic compound at 19.5 ppm. This value is actually the highest for any of the chelating agents. This overabundance of HEDTA, coupled with the unusually high concentration of ED3A, suggests that the waste buried in trench 23M is different than that of most of the waste trenches.

Analytically speaking, detection of HEDTA presented a challenge. In early analyses of the waste

leachates, we detected an unknown species of molecular weight (MW) 288 in the methylated hydrophilic organic fraction. On the basis of GC-MS analysis, it clearly had an ethylenediamine core, but its MW did

graph, we observed that the MW 244 species had a strong IR absorbance at 1690 cm^{-1} , indicating the presence of a lactam ring. The structure that emerged is that of ED3A with one of its acetate

TABLE I
Hydrophilic Organic Compounds^a in Waste Leachates from Maxey Flats

	Waste Trenches (ppb) ^{b,c}							
	7-3	19W	19S	23M	27	33L-4	33L-8	35
Chelating Agents								
Ethylenediaminetetraacetic Acid (EDTA)	5,016	12,364	4,261	4,895	962	402	78	868
N-Hydroxyethylethylenediaminetriacetic Acid (HEDTA)		8,350	888	19,511				
Ethylenediaminetriacetic Acid (ED3A) ^d	1,195	2,190	823	3,884	212			
Dicarboxylic Acids								
Oxalic Acid			111					
Succinic Acid	345		92		26	630	39	80
Methylsuccinic Acid	191				21		21	231
Pentanedioic Acid	248				41		54	406
Hexanedioic Acid	1,569	223	226	244	167	451	104	834
Methylhexanedioic Acid								305
Octanedioic Acid						781	57	
Nonanedioic Acid	455	338	610	210	96	1,394	111	314
Monocarboxylic Acids								
Hexadecanoic Acid								61
Octadecanoic Acid						31	111	
Oxygenated Acids								
4-Oxo-Pentanoic Acid	2,165		241		29		53	185
Aromatic Acids								
Benzoic Acid			635					
2-Hydroxybenzoic Acid							27	
1,3-Benzenedicarboxylic Acid	381	276		440	77			877
1,4-Benzenedicarboxylic Acid	1,181	162		457				1,139
1,2,4-Benzenetricarboxylic Acid	311							
Phthalates								
Dimethyl Phthalate	8,817	2,836	1,772	1,673	391		98	13,565
Methylpropyl Phthalate		213		108	12			874
Diethyl Phthalate					851			

a) Methylated ($\text{BF}_3/\text{Methanol}$), acids identified as methyl esters;

b) No entry indicates compound is below detection levels;

c) Samples collected by BNL in 10/81, except for Trench 27 (10/79); 19S collected by PNL on 7/22/82;

d) Identified as Lactam (MW 244).

not correspond to any known chelating agent. Methylated HEDTA has a MW of 320. Careful interpretation of the GC-MS fragmentation pattern of the MW 288 species revealed the presence of a lactone ring, suggesting that a hydroxyethyl group like that present in HEDTA might be responsible for the lactone formation. GC-MS and MS analysis of methylated HEDTA subsequently revealed that it elutes from a gas chromatographic column only as the MW 288 lactone species.

The third chelating agent identified in the waste leachates is ED3A. It is the least abundant of the three chelating agents and is presumably a degradation product of HEDTA or EDTA via chemical or microbial diagenesis. EDTA has been reported to undergo environmental degradation to ED3A¹³. ED3A does not appear to be commercially available as a chelating agent.

The identification of ED3A also posed an analytical challenge. In the first round of analyses of the waste leachates, we kept identifying an unknown species of MW 244. After careful infrared analysis using a GC-FT-IR instrument, a computerized infrared spectrophotometer interfaced with a gas chromato-

graph, we observed that the MW 244 species had a strong IR absorbance at 1690 cm^{-1} , indicating the presence of a lactam ring. The structure that emerged is that of ED3A with one of its acetate

ligands attached to a nitrogen of the ethylenediamine core to form a lactam ring. This ring closure is undoubtedly a derivatization artifact caused by the heat (100°C) used in the methylation procedure. The species which exists in the aqueous leachates is undoubtedly ED3A in the open, non-lactam form unless the waste had been heated, etc., prior to burial. More research is currently underway to elucidate the mechanism of the lactam formation.

The absence of some of the chelating agents in certain leachates suggests differences in the waste originally buried or, perhaps, in the environment of the trenches. Leachate from trenches 7-3, 27, 33L-4, 33L-8, and 35 lack HEDTA, presumably reflecting differences in the waste. Trenches 33L-4, 33L-8, and 35 also lack ED3A. If ED3A is a degradation product of HEDTA or EDTA, our results indicate that its formation is not a simple process. The leachates that contain the most ED3A (trenches 19W, 19S, and 23M) also contain both HEDTA and EDTA. However, two other samples which contain ED3A (trenches 7-3 and 27) contain only EDTA in addition. In three of the leachates (trenches 33L-4, 33L-8, and 35) EDTA is present without any ED3A.

The other classes of hydrophilic organic compounds consist of a variety of carboxylic acids which are bioorganic compounds or their diagenesis products. Collectively, the carboxylic acids range in concentration from 8.8 ppm in trench 7-3 down to 0.7 ppm in waste trench 27. The dicarboxylic acids are the most abundant acids. One of these acids, oxalic acid, is used in nuclear decontamination operations as a chelating agent, but it is present only in leachate from waste trench 19S at a relatively low concentration of 0.1 ppm. The monocarboxylic acids are poorly represented in the waste leachates. Only two monocarboxylic acids were identified: hexadecanoic acid, commonly known as palmitic acid; and octadecanoic acid, commonly known as stearic acid. Groundwater samples typically contain these two compounds plus a variety of other monocarboxylic acids of increasing and decreasing carbon numbers. The lack of monocarboxylic acids undoubtedly reflects the fact that the water samples are relatively stagnant leachates of buried waste. As a whole, the carboxylic acids are potential complexing agents of radionuclides, but any such association would be expected to be much weaker than the association of radionuclides and the chelating agents. However, these bioorganic acids could well contribute to the formation of fulvic and humic acids, which often comprise most of the dissolved organic carbon (DOC) in groundwater and may be responsible for complexing radionuclides. The importance of such species to the complexation of radionuclides in groundwater is uncertain at this time, but should not be overlooked. Considerable research needs to be carried out on the role of the so-called "natural" organic compounds such as fulvic and humic acids in mobilizing or retarding radionuclide transport in soil solutions.

Hydrophobic Organic Compounds

A variety of hydrophobic organic compounds, presumably all waste-derived, were also identified in the waste leachates from Maxey Flats (Table II). The

concentrations of these compounds are generally much lower than those of the hydrophilic organic compounds (ppb vs ppm). A number of the compounds, e.g., the halogenated hydrocarbons, are toxic and, therefore, of potential environmental concern. Their concentrations are quite low, however. From a research point of view, some of the hydrophobic organic compounds, e.g., the barbiturates, could be exploited as "in-situ," waste-derived tracers of groundwater flow. Organic compounds typically used as "artificial" groundwater tracers, i.e., injected into a groundwater system, such as fluorinated hydrocarbons or organic acids would solvent extract into the hydrophobic organic fraction^{3,14}. It seems clear, therefore, that the amount of information potentially available justifies the research effort in analyzing the hydrophobic organic compounds, even in nuclear-related research.

The two barbiturates, barbital and pentobarbital, are present in leachate from waste trenches 7-3, 19W, 23M and 27. Leachate from waste trench 35 contained only a small amount of pentobarbital, and neither of the barbiturates were present in trenches 33L or 19S. Their source is undoubtedly bio-medical waste. Pentobarbital has been used extensively in pharmacological research, perhaps in conjunction with radioactively labelled tracers. Barbital has been used in the past as a buffering agent in biochemical and clinical research.

The absence of barbiturates in trenches 33L and 19S suggest differences in the waste originally buried in these trenches or, perhaps, in the chemical/biological environment of these trenches. On the other hand, the absence of barbiturates in trench 19S, coupled with their presence in trench 19W, may also be due in part to the way the wastes were originally buried. Several of the waste burial trenches were either intentionally or inadvertently divided into sections by dams, perhaps to segregate different wastes buried in the trenches at different times. Thus, the buried waste, and consequently its leachate

TABLE II
Hydrophobic Organic Compounds in Waste Leachates from Maxey Flats

	Waste Trenches (ppb) ^{a,b}							
	7-3	19W	19S	23M	27	33L-4	33L-8	35
Barbital	48	11		9	35			
Pentobarbital	8	51		8	8			3
Bromodichloromethane			0.2					
Dichloroiodomethane	11	11		1		11		2
Bis(2-Methoxyethyl)Ether				12				
Piperidinone			0.5					
Caffeine	4							
Vanillin						38	26	
Vanillone						3	1	
4-Hydroxybenzaldehyde						1		
Benzotriazole								trace
2(3H)-Benzothiazolone	78	177		53	40			34
Phthalic Anhydride	9	28						trace
Benzoic Acid	3			1	5		1	
Benzene Acetic Acid	7	6		4	7			6
Methylbenzoic Acid				2				
Benzene Propanoic Acid	9	2		7	51	1	2	6
2,5-Dimethyl Benzene Butanoic Acid		39						40
N-Butylbenzene Sulfonamide								4
C ₂ -Toluenesulfonamide			1					
Polyethylene Glycol Oligomers	337							

a) No entry indicates compound is below detection level;

b) Samples collected by BNL in 10/81, except for Trench 27 (10/79); 19S collected by PNL on 7/22/82.

as well, may not be uniform within a particular waste trench. It is not surprising, therefore, that leachates from different sumps in the same burial trench are indeed different. These past burial practices have complicated the research efforts considerably, adding another dimension to the already difficult task of modeling the waste burial site.

Three chemically related compounds, vanillin, vanillone and 4-hydroxybenzaldehyde, were identified in leachates only from trench 33L (sump points 4 and 8). Vanillin (4-hydroxy-3-methoxybenzaldehyde) is commonly used industrially as a flavoring agent in confections, beverages and foods; it appears in perfumes; and is a reagent used in analytical chemistry. Oxidation of vanillin's 4-hydroxy group yields vanilone, whereas elimination of vanillin's 3-methoxy group yields 4-hydroxybenzaldehyde. These two species are likely diagenesis products of vanillin but could well be synthetic by-products of vanillin manufacture. The presence of these three compounds in leachates from trenches 33L-4 and 33L-8, combined with the absence of barbiturates and the low concentrations of chelating agents, argues strongly that the waste buried in trench 33L is quite unique, and perhaps the trench's biological/chemical environment as well. Radionuclide and inorganic research conducted at BNL also indicates that the waste leachate in trench 33L is unique¹⁴.

The remaining hydrophobic organic compounds deserve some mention as well. Two heterocyclic compounds were identified in some of the leachates. The most abundant of these compounds is 2(3H)-benzothiazolone, which appears in leachate from five trenches (7-3, 19W, 23M, 27 and 35). We are not acquainted with the uses of this compound, but the related compound benzotriazole, which appears as a trace constituent in trench 35, is used industrially in the manufacture of rubber and certain pesticides. The 2(3H)-benzothiazolone may be a diagenesis product of benzotriazole, or it may be waste-derived. A series of polyethylene glycol oligomers totalling 337 ppb was identified in leachate from trench 7-3. These compounds are environmentally innocuous and enjoy a wide range of uses in manufacturing. Finally, a number of aromatic carboxylic acids extracted into the hydrophobic organic fraction of the leachates, presumably because the samples had been acidified prior to shipment to our laboratory from BNL. They are undoubtedly microbial diagenesis products.

Association of Organic Compounds with Radionuclides

The presence of relatively high concentrations of strong organic chelating agents like EDTA, HEDTA and ED3A in the Maxey Flats waste leachates prompted a detailed chemical speciation study aimed at determining whether the organic compounds identified in the survey study are chelated or complexed to radionuclides. As outlined earlier, concentrated leachate from waste trench 19S was fractionated by steric exclusion chromatography and subsequently analyzed for its radionuclide and organic content.

The concentrated leachate from trench 19S eluted from the steric exclusion column as several (at least six) distinct UV-absorbing species (Fig. 2). The peaks eluted after the column's void volume indicating that the species are retarded on the column and have nominal MW's less than 1500 based on elution of the column with dextran standards.

GC analyses of the fractions collected during the chromatographic fractionation revealed that EDTA eluted as a bimodal peak in fractions 14-18 (~1.5 -

1.7 hrs)(Fig. 2). Plutonium and ⁶⁰Co co-eluted with the EDTA, strongly suggesting that EDTA is chelated with these radionuclides in the waste leachate. The split peak of EDTA suggests, perhaps, that at least two different types of EDTA-chelates are present. Further detailed organic analyses are needed to determine if the HEDTA and ED3A present in leachate from waste trench 19S are also chelated with the plutonium and ⁶⁰Co.

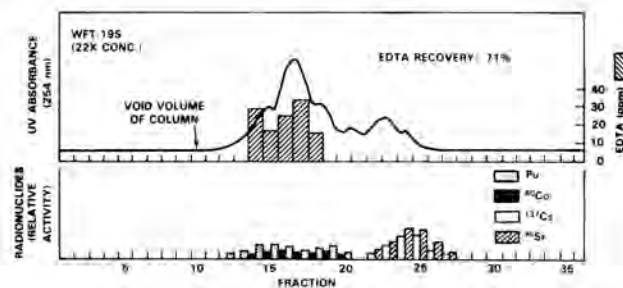


Figure 2. Steric Exclusion Chromatography of Waste Leachate from the Maxey Flats Burial Site.

The above findings agree well with earlier observations that plutonium in leachate from Maxey Flats exists as a strong anionic complex^{4,6,8}. Earlier binding studies with solutions of Pu³⁺, Pu⁴⁺ and EDTA also revealed that the presence of a strong chelating agent like EDTA, even at low concentrations comparable to those in Maxey Flats leachates, may actually be more important than the oxidation state of plutonium in determining whether plutonium adsorbs or migrates in soil⁹. In spite of this, other research at PNL indicates that organic chelation of plutonium and ⁶⁰Co may not be a big problem at Maxey Flats¹⁰. When anoxic leachate from waste trench 27 was exposed to air, the physicochemical forms of these radionuclides changed considerably. Under oxidic conditions, only small fractions of the ⁶⁰Co and plutonium were anionic. Half of the plutonium became cationic. In general, anionic species of radionuclides have been observed to be more mobile in soil compared to cationic forms. Consequently, the changes in the speciation of plutonium and ⁶⁰Co suggest that these radionuclides may become less mobile as they migrate from the anoxic environment of the waste trench and mix with oxygenated groundwater.

A band of ⁹⁰Sr and ¹³⁷Cs activity eluted from the Sephadex G-15 column in fractions 22-27 (2-3 hr). A variety of organic acids and other hydrophilic compounds co-eluted with the ⁹⁰Sr and ¹³⁷Cs. This phenomenon has been observed in a number of groundwater samples, suggesting that there is some sort of electrostatic association between radionuclides and polar organic compounds such as organic acids¹⁴. More research is necessary before the importance of any such association can be assessed.

Concluding Remarks

Organic analyses of the waste leachates at Maxey Flats have revealed that substantial concentrations (ppm levels) of organic chelating agents such as EDTA, HEDTA and ED3A are readily leached from buried waste by water. All of the leachates contained

chelating agents suggesting that their use in nuclear operations has been widespread. Lower concentrations (ppb) of waste-derived hydrophobic organic compounds, including toxic species like barbiturates, are also leachable by water. The presence of ED3A in a number of leachates suggests that the chelating agents can undergo environmental degradation into other chelating agents with strong affinities for radionuclides.

Finally, the detailed chemical speciation study has revealed that EDTA readily chelates with plutonium and ^{60}Co in the leachates, potentially making these radionuclides more mobile in soil solutions. To date, only EDTA has been detected with the radionuclides but it is likely that the other chelating agents present in the leachates, HEDTA and ED3A, are also chelated with the radionuclides. The extent to which the association of organic compounds and radionuclides will impact the environment will, of course, depend on the specific properties of the soil and groundwater at a waste burial site, e.g., oxygen tension, etc.

Much more research needs to be conducted before the importance of organoradionuclide association can be fully assessed in waste leachates, much less in soil solutions. Very little is known, for example, about the complexation of radionuclides to natural organics such as humic and fulvic acids, which often comprise most of the dissolved organic carbon in groundwaters.

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