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CHARACTERIZATION OF ORGANICS IN LEACHATES FROM LOW-LEVEL RADIOACTIVE WASTE DISPOSAL SITES

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ABSTRACT

Several trench leachate samples collected from commercially operated low-level radioactive waste disposal sites at Maxey Flats, Kentucky, and West Valley, New York, were analyzed for organic constituents. The organic compounds in the water samples were extracted with methylene chloride, separated into acidic, basic, and neutral fractions, and analyzed by gas chromatography and mass spectrometry. About 75 compounds consisting of several straight and branched chain aliphatic acids, aromatic acids, alcohols, aldehydes, ketones, amines, aromatic hydrocarbons, esters, ethers, and phenols were identified in the leachate samples. These compounds represent in general the synthetic and natural organic wastes such as contaminated cellulosic materials, scintillation liquids, solvents, and decontamination fluids buried in the trenches and their biological decomposition products. The organic compounds, especially the organic acids, phthalates, and tributyl phosphate, may influence the mobility of the radionuclides from the burial trenches by solubilization, leaching, and formation of weak complexes.

INTRODUCTION

Low-level radioactive wastes generated by the nuclear industry, universities, research institutions, and hospitals are disposed of in shallow-land trenches and pits. In 1962 the first commercial disposal site was opened in Beatty, Nevada. Since then, the industry has grown to include three private companies operating six disposal areas located in sparsely populated areas: at Maxey Flats (Morehead), Kentucky; Beatty, Nevada; Sheffield, Illinois; Barnwell, South Carolina; West Valley, New York; and Richland, Washington. Although the facilities are operated by private industry, they are located on public land and are subject to federal and state regulation. A comprehensive summary of the shallow-land radioactive waste burial operations, classification of wastes, and projections of burial capacities of the existing commercial sites has been presented by Holcomb (1978).

The burial sites were selected in part because the hydrogeological formations were expected to contain the waste material; however, leakage of radionuclides has been reported at two of these sites. In 1975 the facility at West Valley, NY, was closed because tritium and ^{90}Sr were leaking from the burial trenches (Nucleonics Week, 1975). At Maxey Flats, KY, plutonium has been identified in the soil and water samples collected at the burial site and its environs (Meyer, 1976). Furthermore, radionuclide migration has been found also at other burial facilities operated by the U.S. Department of Energy (Hanford, WA; Savannah River, SC; Oak Ridge, TN; and at the Canadian burial site at Chalk River (Means, et al., 1978). Thus, the problem of migration of radioisotopes from existing burial sites appears to be pervasive, and the causes are being investigated because of the serious problems of environmental contamination from unsafe burial techniques.

Although inventories of the radioactive materials buried in the disposal sites are available, no specific records are kept on the kinds and quantities of organic wastes buried. In general, the organic wastes consist of contaminated paper, packing materials, clothing, plastics, ion-exchange resins, scintillation vials, solvents, chemicals, decontamination fluids, carcasses of experimental animals, and solidification agents. Radionuclides such as ^{14}C, ^{3}H, ^{90}Sr, $^{134,137}Cs$, ^{60}Co, ^{241}Am, and $^{238,239,240}Pu$ have been identified in leachate samples collected from several trenches at Maxey Flats and West Valley (Weiss et al., 1979; Husain et al., 1979). The purpose of this report is to identify some of the organic compounds present in high concentrations in trench leachates at the disposal sites in order to begin to evaluate their effect on radionuclide mobilization and contamination of the environment.

EXPERIMENTAL

Water samples from the shallow-land low-level radioactive waste burial sites at Maxey Flats, KY, West Valley, NY, Sheffield, IL, and Barnwell, SC, were collected to determine the dissolved organic carbon (DOC) content. Samples were taken from the trenches and from monitoring wells usually located around the periphery of the sites. These samples were filtered through a 0.45-μ silver membrane filter and transferred to thoroughly cleaned and sterilized glass bottles fitted with Teflon-lined screw caps. The samples were placed in ice and shipped to the laboratory for DOC analysis.

The total carbon and inorganic carbon contents of the filtered water samples were determined with a Beckman total carbon analyzer (Beckman Instruments, Inc., Fullerton, CA); the difference between the total and the inorganic carbon yielded the dissolved organic carbon content.

Leachate samples for detailed organic analysis were collected under anoxic conditions in clean one-gallon borosilicate glass bottles sealed by Teflon valves. The procedure and apparatus for collecting the water from trenches has been described previously (Weiss et al., 1979). The filled bottles were shipped in ice and, upon receipt at the laboratory, were refrigerated at 4°C. The samples were filtered through a 0.45-μ silver membrane filter under anoxic conditions and then used to determine the DOC and the organic constituents.

A liquid extraction technique (Garrison et al., 1976) was used to isolate acidic, neutral, and basic organic components from trench water samples collected at the Maxey Flats, KY, and West Valley, NY, burial sites. Approximately 200 to 500 ml of a filtered water sample was acidified to pH 2.0 with HCl and extracted three times with 30-ml portions of methylene chloride (Burdick & Jackson Laboratories, Inc., Muskegon, MI). The extracts were combined and back-extracted two times with 50 ml of 5% w/v NaOH, to remove acidic components, leaving only neutral compounds in the first organic extract. The basic fractions were combined, acidified to pH 2.0, and extracted with methylene chloride as before. This second organic extract contains acidic compounds. Next the original water sample was brought to pH 11.0 with 50% w/v NaOH, and extracted three times with 30 ml of methylene chloride. The third extract contains basic organic components. Each extract was dried over anhydrous Na_2SO_4 and concentrated to 1 ml in Kuderna-Danish and Micro-Snyder column evaporators. The extract containing the acid components was divided in half, and one portion was reacted with N,O,bis-(trimethylsilyl)-trifluoroacetamide (Pierce Chemical Co., Rockford, IL) to form the trimethylsilyl derivatives of the organic components. A control blank sample consisting of the same amounts of reagents and solvent was run through the entire extraction and analytical scheme for each sample set.

The extracts, derivatized extracts of water samples, and control blank samples were analyzed by gas-liquid chromatography (GLC) on a Perkin Elmer model 900 gas chromatograph equipped with a flame ionization detector. A 1.8-m x 2.1-mm-i.d. stainless steel column packed with 10% SE-30 on 80/100 mesh Chromosorb-W was used for all analyses. Helium was used as the carrier gas at a flow rate of 35 ml/min. During each run the column temperature initially was held constant at 60°C for 4 min and then programmed to 240°C at 4°C/min. The upper temperature was maintained until the analysis was terminated. For quantitative analysis a known quantity of an internal standard, usually diethyl phthalate, was added to the sample. The ratio of the area of the GLC peak of interest to the area of the internal standard peak was converted to a concentration by a calibrated standard curve constructed specifically for the compound undergoing analysis.

The water extracts were further analyzed by gas chromatography-mass spectrometry (GS/MS) to identify the various organic compounds. A Hewlett Packard 5984A mass spectrometer consisting of a HP 5700 gas chromatograph and a HP 5933 data system was used. The gas chromatograph and mass spectrometer are interfaced by a heated glass jet separator. Gas chromatographic conditions were the same as listed previously, except that a 2-mm-i.d. glass column was used. Mass spectral identification was facilitated by use of the HP Contributed Libraries, the EPA-NIH Library, and the mass spectral search facilities of the Chemical Information System. In some cases, known standards were purchased commercially and run on the GC/MS instrument in order to verify identifications.

RESULTS AND DISCUSSION

The results of an initial survey of the dissolved organic carbon content of trench leachates and well water samples collected from four low-level radioactive burial sites are shown in Table 1. The range of values may be compared with the value for unpolluted groundwater, which is reported by most investigators to be between 5 and 30 ppm and usually less than 10 ppm. Clearly, both trench and well water samples contain dissolved organic carbon, but the trench leachates contain considerably more except in the case of Sheffield, IL.

A comprehensive list of all organic compounds that have been identified in trench leachates from the West Valley and Maxey Flats sites is given in Table 2. It should be noted that not all compounds can be extracted by methylene chloride, and probably many other organic compounds are present in the leachates. The organic compounds found consisted of several straight- and branched-chain aliphatic acids, aromatic acids, alcohols, aldehydes, ketones, amines, aromatic hydrocarbons, esters, ethers, and phenols.

Typically, the acidic fraction of the samples contained several compounds, the neutral fraction contained fewer compounds, and the basic fraction, except in the case of one or two trench leachate samples, yielded no detectable compounds. This may be due to the limitation of using a gas chromatographic column not specifically selected for the detection of basic compounds. Quantitative results on the numerous compounds detected in Maxey Flats and West Valley samples are shown in Tables 3 and 4, respectively. The concentrations reported are those found in the methylene chloride extract and not those in the original water sample. Note that the solvent extraction efficiency for each compound in

such a complex aqueous solution and the possible matrix effects were not determined. It is interesting that in many cases two samples of a trench leachate taken a year apart contained identical and similar types of major compounds, although some quantitative variations between the two samplings were generally observed.

The types of organic compounds identified in the trench leachates reflect both the nature of the buried waste and the products of biodegradation. For example, p-dioxane, toluene, and xylene may be discarded solvents or scintillation fluids. Tributylphosphate may originate from the process of solvent extraction of metal ions from solutions of reactor products, and low molecular weight straight- and branched-chain aliphatic acids are due mainly to microbial degradation of complex natural and synthetic materials in the buried waste.

Some mechanisms of radionuclide migration have been examined by de Marsily et al. (1977), including transport in groundwater by convection, diffusion and sorption phenomena. These mechanisms are complicated by the ability of radionuclides to form stable complexes with organic compounds that are buried with the radioactive waste, are naturally present, or result from microbial action. Studies with heavy metals and naturally occurring humic acid have shown the formation of soluble metal complexes which may be important in mobilization (Takamatsu and Yoshida, 1978; Zurino and Martin, 1977). Likewise, soil microflora metabolites may be an important source of agents that affect the long-term solubility characteristics of transuranic elements (Wildung et al., 1977). Bolter et al. (1975) reported that organic acids from decaying leaf litter in soil increased the solubility of heavy metals deposited from smelters. Recently, Means et al., (1978) found that ethylenediaminetetraacetic acid was the dominant mobilizing

agent of ^{60}Co and U from intermediate-level liquid waste disposal pits and trenches at the Oak Ridge burial grounds. They also showed that organic ligands can have pronounced effects by reducing the absorption capacity of soil for radionuclides. Since only strong chelating agents were studied, the effect of weak complexing agents remains unexamined but could be significant over the lifetime of the radionuclides. The finding of several organic acids in the leachates and the possible presence of synthetic and natural chelating agents in the waste strongly indicate the potential for migration of radionuclides from the burial trenches, and warrant further examination.

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Table 1.

Distribution of Water Samples from Low-level Radioactive Waste Disposal Sites According to Dissolved Organic Carbon Content.

Sample Source	Total Number of Samples	Number of Samples with DOC Content (mg/ℓ) of: 2-10	10-100	100-1000	1000-7000
Maxey Flats, KY					
Trench	46	2	10	23	11
Wells	10	10	-	-	-
West Valley, NY					
Trench	13	-	-	4	9
Wells	10	8	2	-	-
Sheffield, IL					
Trench	1	-	1	-	-
Wells	26	-	4	13	9
Barnwell, SC					
Trench	9	4	2	3	-
Wells	3	3	-	-	-

Table 2.

Compounds Identified in Trench Leachates
from Maxey Flats and West Valley Disposal Sites

Acids:

Benzoic acid
Butanoic acid
Decanoic acid
2-Ethylhexanoic acid
Hexanoic acid
Hydroxybenzoic acid
3-Methoxy-4-hydroxybenzoic acid
2-Methylbutyric acid
3-Methylbutyric acid
2-Methylhexanoic acid
2-Methylpentanoic acid
3-Methylpentanoic acid
2-Methylpropionic acid
Nonanoic acid
Octanoic acid
Pentanoic acid
Phenylacetic acid
Phenylbutyric acid
Phenylhexanoic acid
Phenylpropionic acid
Toluic acid (isomers)

Alcohols:

Borneol
2-Butanol
Cyclohexanol
2-Ethylhexanol
3-Ethylhexanol
2-Hexanol
3-Hexanol
2-Methyl-2-butanol
Methylcyclohexanol
Octanol
2-Phenylcyclohexanol
$(\text{Propylene glycol})_n$
α-Terpineol
3,3,5-Trimethylcyclohexanol

Aldehydes and Ketones:

p-Hydroxybenzaldehyde
Paraldehyde
Vanillin
Acetovanillon
Camphor
Diacetone alcohol
Dibutyl ketone
Fenchone
Methyl ethyl ketone
Methyl isobutyl ketone

Table 2.
(Cont'd)

Compounds Identified in Trench Leachates
from Maxey Flats and West Valley Disposal Sites

Amines:

Aniline
Cyclohexylamine
Dicyclohexylamine
Methyldicyclohexylamine

Aromatic Hydrocarbons:

Benzene
Biphenyl
Dimethylnaphthalene
Naphthalene
Toluene
Xylene (isomers)

Esters:

Butyl phthalate
Diethyl phthalate
Several unidentified phthalates
Tributyl phosphate
Triethyl phosphate
Triphenyl phosphate

Ethers:

Anisole
Bis(2-chloroethyl) ether
Bis(2-chloroethoxy) methane
Bis(2-ethoxyethyl) ether
1,1-Diethoxyethane
1,1-Diethoxy-2-chloroethane
1,4-Dioxane
Tetrahydrofuran
Tripropylene glycol methyl ether

Phenols:

Cresol (isomers)
Octylphenol
Phenol
4-t-Butylphenol
Tetramethylbutylphenol

Table 3.

Organic Compounds Identified in Maxey Flats
Trench Leachate Samples

Compound	Concentration (mg/ℓ) Trench 19	Trench 26	Trench 32
Acids:			
Benzoic acid	0.22	1.2	1.9
2-Ethylhexanoic acid	5.6	3.4	8.8
C_8 branched acids*	1.4	-	-
Hexanoic acid	1.5	1.9	4.7
2-Methylbutyric acid	4.6	19	13
3-Methylbutyric acid	1.8	-	5.8
2-Methylhexanoic acid	1.5	1.2	3.2
3-Methylpentanoic acid	3.1	4.2	4.0
C_6 branched acid**	0.33	-	1.4
2-Methylpropionic acid	0.40	3.6	2.6
Octanoic acid	0.36	-	1.3
Pentanoic acid	2.0	4.6	4.7
Phenylacetic acid	0.56	1.5	3.4
Phenylhexanoic acid	+	+	+
Phenylpropionic acid	1.2	1.3	9.8
Others:			
Cresols (isomers)	2.9	2.0	4.2
Cyclohexanol	0.38	-	0.24
Dibutyl ketone	+	-	-
Diethyl phthalate	-	0.08	-
p-Dioxane	+	+	+
Fenchone	0.03	-	-

Table 3.
(Cont'd)

Organic Compounds Identified in Maxey Flats
Trench Leachate Samples

Compound	Concentration (mg/ℓ) Trench 19	Trench 26	Trench 32
Others (Cont'd):			
Methyl isobutyl ketone	+	-	-
Naphthalene	0.12	0.28	0.28
Phenol	-	-	1.2
Phthalate (unknown)	-	-	+
α-Terpineol	-	0.31	0.49
Toluene	2.9	3.5	6.9
Tributyl phosphate	0.16	-	0.36
Triethyl phosphate	0.03	-	-
Xylene (isomers)	0.12	-	0.48

- = Not detected.

+ = Compound present but not quantified.

* = Quantified by using 2-ethylhexanoic acid standard.

** = Quantified by using 3-methylpentanoic acid standard.

Table 4.

Organic Compounds Identified in West Valley Trench Leachate Samples

Compound	Concentration (mg/ℓ) Trench 3	Trench 5	Trench 8
Acids:			
Benzoic acid	5.8	13	6.7
Decanoic acid	0.87	2.6	1.1
2-Ethylhexanoic acid	105	89	216
Hexanoic acid	22	43	65
Hydroxybenzoic acid	-	+	-
2-Methylbutyric acid	88	60	189
3-Methylbutyric acid	-	17	+
2-Methylhexanoic acid	7.5	8.2	14
C_6 branched acid*	14	12	20
3-Methylpentanoic acid	-	1.6	2.1
2-Methylpropionic acid	12	15	21
Nonanoic acid	2.0	5.1	6.4
Octanoic acid	6.4	19	20
Pentanoic acid	30	40	73
Phenylacetic acid	3.8	7.5	6.0
Phenylhexanoic acid	+	+	+
Phenylpropionic acid	9.4	8.6	15
Toluic acid	-	0.78	0.63

Table 4.
(Cont'd)

Organic Compounds Identified in West Valley
Trench Leachate Samples

Compound	Concentration (mg/ℓ) Trench 3	Trench 5	Trench 8
Others:			
Anisole	-	2.7	-
Butyl phthalate	+	-	-
Cresol (isomers)	3.4	3.4	4.2
Cyclohexanol	-	0.59	-
p-Dioxane	+	+	+
2-Ethyl-1-hexanol	8.1	3.6	5.7
Fenchone	-	-	0.14
Naphthalene	-	1.7	0.46
Octyl phenol (isomer)	+	-	-
Phenol	-	9.5	0.88
Phthalate (unknown)	-	-	+
α-Terpineol	-	-	0.64
Toluene	1.9	18	4.8
Tributyl phosphate	0.35	0.76	0.86
Tripropylene glycol methyl ether	+	+	+

- = Not detected.

+ = Compound present but not quantified.

* = Quantified by using 3-methylpentanoic acid standard.