Jan 29, 1981

BNL-NUREG-27939

TITLE: Trench Water-Soil Chemistry and Interactions
at the Maxey Flats Site *
Allen J. Weiss and Kenneth S. Czyscinski
Brookhaven National Laboratory, Upton, N.Y. 11973

Summary:

This report is part of an overall program designed to provide an understanding of and to monitor the behavior of existing low-level sites. This investigation will provide source term data for radionuclides and other solutes in trench waters and will describe the physical, chemical, and biological properties of the geochemical system that controls radionuclide movement.

General conclusions can be made from the data in terms of source term information to be used in modeling efforts, as well as processes which may affect radionuclide migration.

Trench waters are complex anoxic chemical systems which require more extensive investigation to assess their role in radionuclide retention and mobilization. No overall systematic changes in the disposal site trenches were observed during the brief sampling interval. However, changes in some radionuclide and cation concentrations were observed in several trenches. Numerous organic compounds were identified in trench waters at Maxey Flats, some of which have the potential for chelation with radionuclides.

The presence of radionuclides and organic compounds in wells UB1 and UB1-A and in nearby trenches indicates communication between the wells and trench water leachates by subsurface migration. Radionuclides were also measured in the new experimental trench dug parallel to trench 27.

Aerobic, anaerobic, sulfate reducing, denitrifying, and methanogenic bacteria are present in the leachate samples, and are able to grow anaerobically in trench leachates.

Experimental results indicate that the observed sorption K_d is a function of both solid and liquid phase compositional variations as well as contact time. The observation that the lowest K_d results are observed with anoxic trench waters and ultrasonicated soils points to the need to

---

*This work was performed under the auspices of the Nuclear Regulatory Commission.

use site specific materials and experimental conditions which simulate in situ conditions as closely as possible.

Introduction:

This report concerning the Maxey Flats, Kentucky, site is part of an overall program designed to provide experimental research support to the U.S. Nuclear Regulatory Commission in the development of criteria for the selection and licensing of solid low-level radioactive waste disposal sites. One of the significant factors in the development of these criteria is the ability to make predictions on the rate of movement of radionuclides along the groundwater flow path. This study attempts to provide an understanding of and to monitor the behavior of existing low-level disposal sites.

In cooperation with the U.S. Geological Survey, a field and laboratory program was initiated to study the existing commercial low-level radioactive waste disposal sites. This investigation will define the source terms (concentrations in solutions) for radionuclides and other solutes in trench waters at the sites, and will describe the physical, chemical, and biological properties of the geochemical system that control the movement of radionuclides.

Three major areas of study are included in this program: (i) trench water analysis, (ii) microbiological processes, and (iii) geochemical considerations.

Trench Water Analysis

Procedures for the collection, preparation and analysis of trench waters were developed when necessary, to supplement standard procedures. Inorganic, organic, and radiochemical constituents in trench waters are being measured and their relevance to movement of radionuclides is being evaluated. Water from test wells in and around the disposal sites are being sampled to detect and characterize radionuclides along the flow paths of groundwater.

Microbiological Processes

Microbial degradation of organic material buried in the trenches may contribute directly or indirectly to the migration of radionuclides. The consequences of the interaction of radionuclides present in the trenches with the products of microbial activity are being measured and evaluated, e.g., gas generation and formation of soluble organo-radionuclide complexes.

Geochemical Considerations

The geochemical aspects of radionuclide migration and retention treated in this portion of the program are limited to laboratory sorption studies, involving batch and column experiments using site-specific materials and performed under conditions which simulate the field situation. Data and ideas developed from these studies will be compared to the results of core analysis for field verification. Conclusions derived from these studies are expected to have direct application to modeling studies of some of the sites and to establish siting criteria and improved burial practices at future sites.

Experimental Approach:

The objective of the analytical program is to measure the concentrations of radionuclides and other chemical species present in trench waters. Procedures were designed to maintain the anoxic nature of the trench waters during collection, storage, and subsequent handling. A schematic diagram of the water collection system is shown in Figure 1. Oxygen leaking into the samples will result in the formation of an iron (ferric) hydroxide precipitate. After collection, the water samples are stored in 4-liter borosilicate glass bottles designed to maintain the trench water environment. The anoxic collection procedure allows samples to be stored for months without visible signs of the reddish-brown ferric hydroxide that forms after exposure to air.

Selected physico-chemical characteristics of trench waters, which are subject to change during storage, are measured at the time of sample collection. The temperature, pH, redox potential (Eh), dissolved oxygen, and specific conductance of the trench water samples are measured in-line while the water sample is being collected.

Upon arrival at BNL, the trench water samples are filtered through 0.45 μm membrane filters to remove particulate matter present in them. The filtering process is also done under an inert atmosphere to maintain the anoxic character of the waters. The filtrate is divided into several fractions and processed according to the scheme shown in Figure 2.

Trench waters are analyzed for major inorganic constituents using ion specific electrodes, colorimetric, and atomic absorption methods. Organic compounds are determined by solvent extraction followed by gas chromatographic and mass spectrometric analyses. Radiochemical analyses are performed by gas flow proportional counting (alphas and betas), liquid scintillation counting (tritium), Ge(Li) gamma-ray spectroscopy, and radiochemical separations (strontium-90 and plutonium isotopes). The particulate fraction is analyzed for radiochemical constituents only.

Site specific batch K_d studies are performed with Maxey Flats soil and trench waters under inert atmosphere to simulate the anoxic conditions in the trenches. The initial K_d measurements were intended for scoping studies to determine the K_d dependency as a function of (i) pH, (ii) soil/water ratio, (iii) water composition, (iv) oxic vs anoxic water regimes, (v) soil composition (ground/sieved vs untreated soils), and (vi) time.

The general method of preparing samples for K_d measurements is to add radionuclide spikes to filtered trench water, and to perform a series of anoxic operations (pH adjustment, dilution, and transfer to reaction vessel containing soil), with a manifold or in a glove box. To equilibrate the soil and water, the samples are tumbled in an apparatus, designed to maintain an anoxic environment. The activity remaining in the liquid phase is determined by gamma-ray spectroscopy.

Details of the procedures described above are reported elsewhere (Weiss, et al., 1980).

Results and Discussion:

Trench Water Analyses

Results of the analyses of several trench and well water samples collected from the Maxey Flats disposal site between September 1976 and May 1978 are shown in Tables 1-3. The location of trenches and wells are shown in Figure 1 of the executive summary. Additional data from Maxey Flats and results of similar measurements from the West Valley, New York; Sheffield, Illinois; and Barnwell, South Carolina, disposal sites are reported elsewhere (Weiss, et al., 1980).

Trench waters are complex water systems as illustrated by the shapes of acid-base titration curves in Figure 3. The curve obtained with water from well UB1-A resembles a typical simple groundwater.

No overall systematic changes in the disposal site trenches were observed during the brief sampling interval. However, changes in some radionuclide and cation concentrations were observed in several trenches. Tritium was the most abundant of the radionuclides and was found in all the trench waters. Chemically bound as HTO, tritium would be the most mobile radionuclide. ^{90}Sr, ^{238,239,240}Pu and ^{173}Cs were found as dissolved species in all trench waters and sorbed on suspended particulates.

Results of the GC/MS analyses of water from trench 19S, trench 32, and well UB1 are shown in Table 2. The organic compounds found in the trench waters consisted of straight- and branched-chain aliphatic acids, aromatic acids, alcohols, aldehydes, ketones, amines, aromatic hydrocarbons, esters, ethers, and phenols. The types of compounds identified reflect both the nature of the buried waste and the products of biodegradation.

A comparison of organics identified in well UB1 and trench 32 shows that every compound in well UB1, except tolulic acid, is present in trench 32, and a majority of these compounds are present in trench 19S. Other nearby trenches, which were not sampled, may also contain these compounds. The presence of radionuclides and organic compounds in wells UB1 and UB1-A and also in nearby trenches indicates communication between the wells and trench water leachates, and that migration of radionuclides from trenches has occurred.

To determine the movement of radionuclides by subterranean routes on the site, a new experimental trench was dug parallel to trench 27 to intercept water flowing from the burial trench area. Partial analysis of water collected 10/30-11/2/79 (a few weeks after completion of the trench) from four of the five sections are shown in Table 3. Also shown are the analyses of water taken during the same sampling period from the burial trenches and an observation well. Only trench section T-2E had sufficient water to obtain in-line measurements. Alpha, beta, tritium, strontium-90, and plutonium-238,239,240 radioactivities were measured in the four trench sections. Section T-2E appears to have the most radioactivity, and also contains 120 mg/L of DOC, which is more than an order of magnitude greater than the DOC measured in well UB1-A. GC/MS analyses of the organics in T-2E indicate a few small components including Phenol, Dioxane, C-8 acids, and 2-Ethylhexanol.

Microbiological Processes

The microbiological study found that: (i) aerobic and anaerobic bacteria, sulfate reducing, denitrifying, and methanogenic bacteria are present in the leachate samples, (ii) the bacteria identified are *Bacillus* sp., *Pseudomonas* sp., *Citrobacter* sp., and *Clostridium* sp., (iii) mixed bacterial cultures isolated from the trench leachates are able to grow anaerobically in trench leachates, which indicates that the radionuclides and organics present in leachates are not toxic to these bacteria, (iv) the organic compounds in the leachates are utilized by the bacteria as a carbon source for growth, (v) preliminary studies on the anaerobic degradation of organic compounds of the leachate sample indicate that several of the organic compounds are being both synthesized and destroyed by these bacteria, and (vi) methane bacteria present in the leachate samples produced appreciable amounts of tritiated and carbon-14 methane from the leachates.

Sorption Studies - K_d

Sorption studies indicate that K_d varies as a function of the experimental design. Variations of the parameters discussed in the experimental section all affected the measured K_d values. Sorption K_d curves for ^{241}Am, shown in Figure 4, illustrate the dependence on time and experimental conditions, e.g., #4 and #5 reached a steady state early, #3 was still increasing after 1900 hours, and #1 and #2 exhibited a rise until 800 hours. The variability of K_d measured with different waters from the site under the same experimental conditions is illustrated by waters from trench 19S, trench 27, and well UB1-A (#1 vs #4 vs #3). Similar sorption data for other radionuclides are reported in Weiss, et al., 1980.

Sorption coefficients for combinations of soil and trench water conditions are shown in Table 4. The lowest K_d was obtained with ultrasonicated soil and anoxic trench water. These results emphasize the necessity for conducting K_d experiments under site specific conditions. To get the most realistic K_d estimates actual conditions must be simulated as closely as possible.

Future sorption work will involve some batch experiments, and will also involve flow-through column experiments, which more closely simulate the field situation. Batch experiments will be designed to allow comparison with column experiment results, and provide information of a mechanistic nature which will be useful in predictive applications.

References:

A. J. Weiss, P. Colombo, J. H. Clinton, K. S. Czyscinski, S. Dobbs, R. F. Doering, A. J. Francis, G. G. Galdi, S. L. Garber, C. L. Green, C. R. Iden, B. J. Nine, R. F. Pietrzak, and J. Steiners, Brookhaven National Laboratory, "Evaluation of Isotope Migration-Land Burial, Water Chemistry at Commercially Operated Low Level Radioactive Waste Disposal Sites," NUREG/CR-1289, BNL-NUREG-51143, 1980.

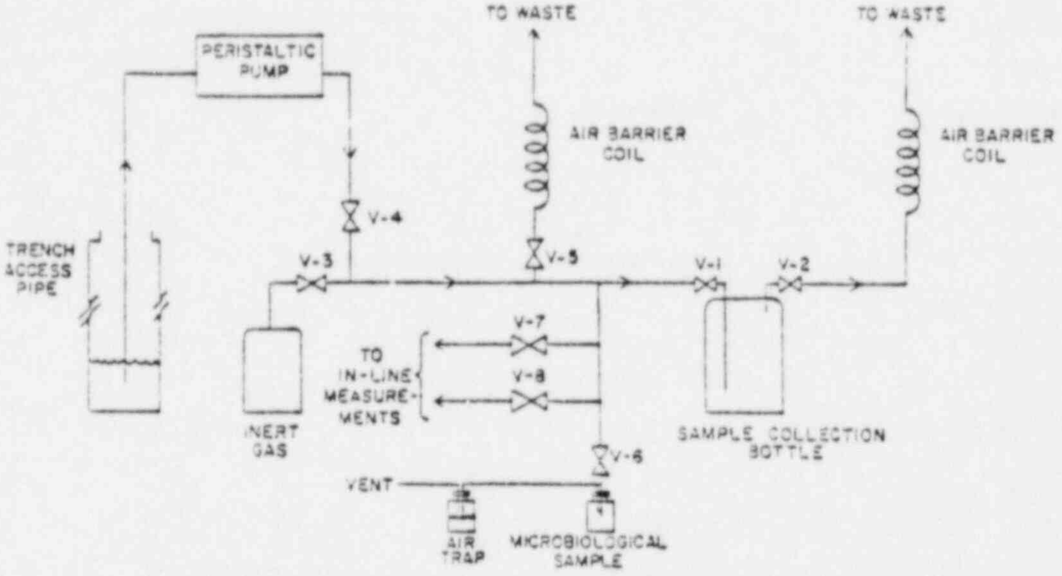

Figure 1. Schematic diagram of the system for anoxic collection of water.

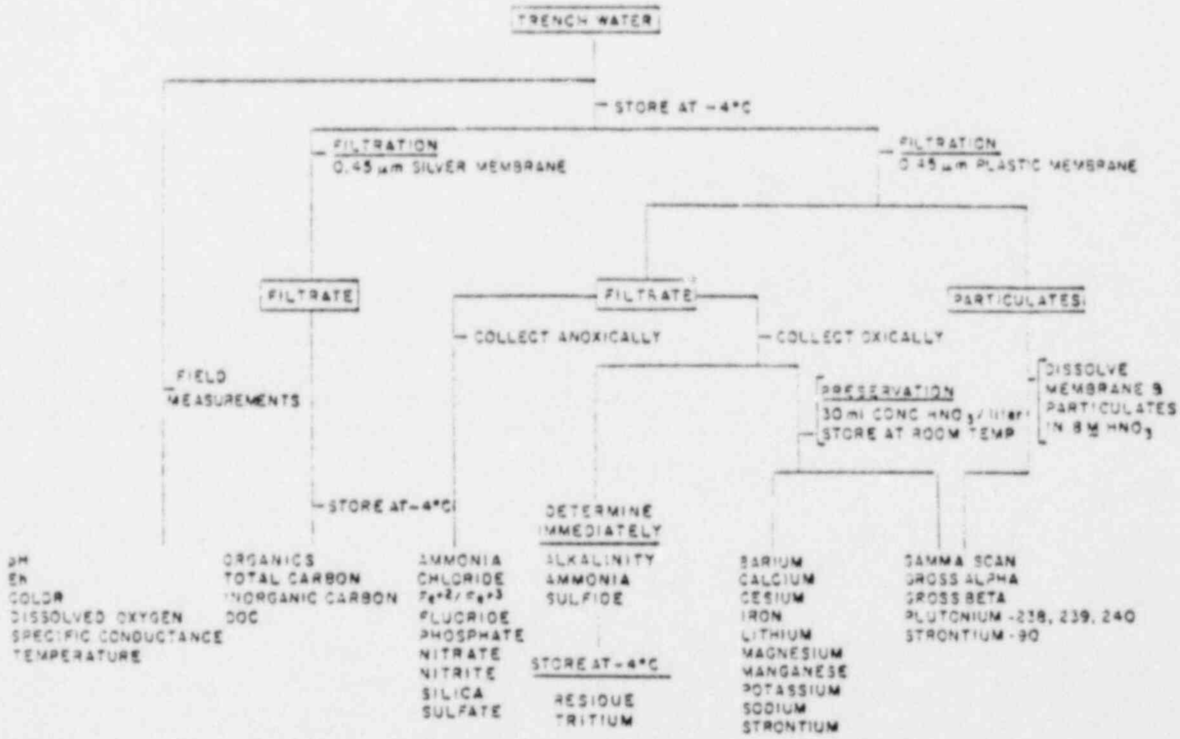

Figure 2. Scheme for partitioning water samples for analysis.

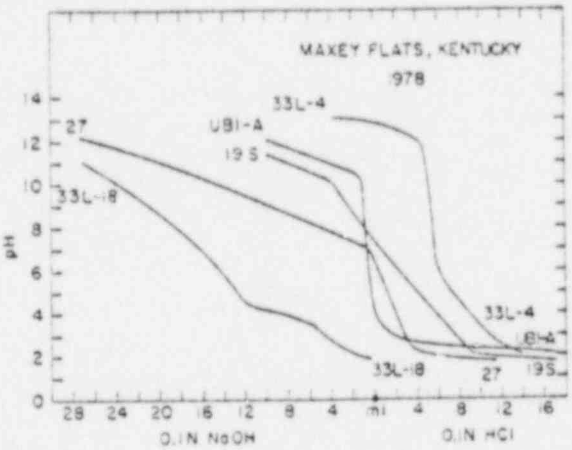

Figure 3. Acid-base titration curves of water samples from Maxey Flats, Kentucky, disposal site, May 1978.

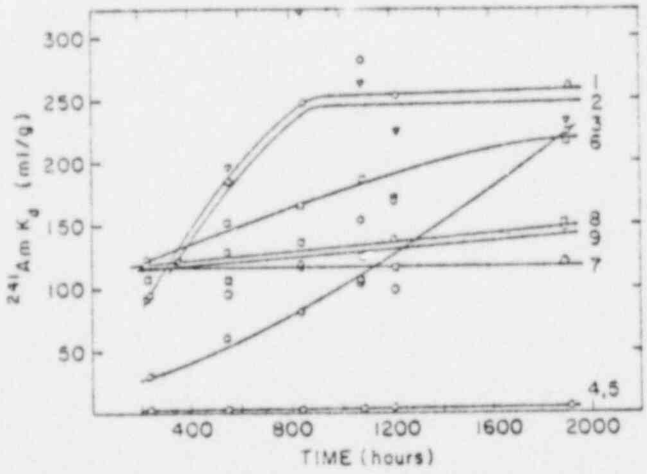

Figure 4. ^{241}Am K_d sorption coefficient versus time for waters and soils from Maxey Flats, Kentucky, Disposal Site.

Water: Oxic
Soil: Ultrasonicated
Solution/soil ratio: 20 mL/g
Reaction Container: TFE Teflon

Experiment	MF Code	Water	Soil
1	155	19S	shale
2	155	19S	sandstone
3	156	Well UB1A	shale
4	157	27	shale
5	157	27	sandstone
6	158	33L-4	shale
7	158	33L-4	sandstone
8	159	33L-18	shale
9	159	33L-18	sandstone

Table 1

Concentration of Dissolved Radionuclides in Water Samples
Taken From Maxey Flats, Kentucky, Disposal Site

pCi/L (±2σ%) [a]

Radionuclide	Date	Trench 2	Trench 195[b]	Trench 26	Trench 27	Trench 32	Trench 33L-4[f]	Well UB1-A
Gross Alpha	9/76	1.2 E4 (4.3)	2.3 E5 (<1)	4.1 E4 (2.7)	4.8 E4 (2.3)	8.6 E4 (1.4)	7.6 E3 (5.2)	---
	7/77	6.7 E3 (8.5)	---	2.7 E4 (4.0)	---	3.1 E4 (3.9)	---	---
	5/78	---	1.7 E5 (1.7)	---	4.9 E3 (11)	---	4.9 E3 (13)	<10
Gross Beta	9/76	2.8 E4 (3.6)	7.5 E5 (<1)	1.3 E5 (1.6)	7.2 E5 (<1)	1.2 E6 (<1)	7.0 E4 (1.9)	---
	7/77	2.4 E4 (5.5)	---	1.2 E5 (1.2)	---	1.8 E6 (<1)	---	---
	5/78	---	6.4 E5 (2.0)	---	4.0 E5 (2.6)	---	3.7 E4 (8.8)	3.1 E2 (30)
Tritium	9/76	2.5 E7 (<1)	6.9 E7 (<1)	2.0 E8 (<1)	3.1 E8 (<1)	2.1 E8 (<1)	6.2 E7 (<1)	---
	7/77	2.1 E7 (<1)	---	1.3 E8 (<1)	---	2.3 E9 (<1)	---	---
	5/78	---	6.8 E7 (<1)	---	5.9 E8 (<1)	---	2.9 E7 (<1)	5.8 E6 (<1)
$^{90}Sr^{d}$	9/76	6.8 E3 (<1)	2.6 E5 (<1)	3.5 E4 (<1)	2.0 E5 (<1)	3.8 E5 (<1)	2.4 E4 (<1)	---
	7/77	3.6 E3 (10)	---	3.0 E4 (10)	---	5.4 E5 (<10)	---	---
	5/78	---	2.9 E5 (10)	---	2.1 E5 (10)	---	1.7 E4 (10)	6.3 E1 (10)
$^{238}Pu^{d}$	9/76	3.8 E3 (2.7)	1.7 E5 (7.6)	3.1 E4 (6.8)	1.3 E4 (3.1)	3.6 E3 (4.2)	9.9 E3 (4.4)	---
	7/77	9.4 E3 (10)	---	1.3 E5 (10)	---	1.1 E5 (10)	---	---
	5/78	---	2.1 E5 (10)	---	4.1 E3 (10)	---	4.2 E2 (10)	1.4 E1 (16)
$^{239,240}Pu^{d}$	9/76	4.1 E2 (8.6)	2.1 E4 (24)	2.7 E3 (2.2)	1.7 E3 (13)	1.1 E2 (25)	8.4 E2 (40)	---
	7/77	2.8 E2 (10)	---	3.5 E3 (10)	---	2.9 E3 (10)	---	---
	5/78	---	8.4 E2 (10)	---	6.7 E2 (10)	---	6.6 E3 (10)	5.4 E-1 (110)
^{241}Am	9/76	4.3 E3 (3.9)	7.7 E2 (7.0)	1.0 E3 (5.7)	1.5 E4 (3.8)	<40	<20	---
	7/77	2.9 E3 (8.9)	---	N.D.[e]	---	N.D.	---	---
	5/78	---	1.5 E3 (17)	---	1.4 E3 (17)	---	N.D.	N.D.
^{60}Co	9/76	1.4 E4 (1.9)	1.3 E3 (23)	1.3 E3 (6.8)	2.0 E4 (3.2)	6.0 E3 (5.6)	<300	---
	7/77	1.0 E4 (4.5)	---	1.4 E3 (14)	---	3.5 E3 (8.1)	---	---
	5/78	---	2.5 E3 (11)	---	1.3 E3 (21)	---	3.6 E1 (64)	2.5 E2 (13)
^{134}Cs	9/76	<100	<100	3.1 E2 (18)	<100	4.2 E2 (24)	<100	---
	7/77	N.D.	---	N.D.	---	N.D.	---	---
	5/78	---	N.D.	---	N.D.	---	N.D.	N.D.
^{137}Cs	9/76	<100	3.2 E3 (9.8)	7.5 E3 (2.0)	2.3 E4 (2.4)	6.0 E3 (4.6)	<100	---
	7/77	N.D.	---	5.3 E3 (5.7)	---	4.8 E3 (5.5)	---	---
	5/78	---	1.0 E4 (3.8)	---	8.0 E3 (4.6)	---	2.1 E2 (66)	N.D.

[a] Number in ( ) = 2σ percent counting uncertainty.

[b] Trench 19S sample collected 9/76 contained 2.3 E1 (11) pCi/L ^{22}Na in addition to radionuclide listed in table.

[c] --- indicates sample was not collected from trench on indicated date.

[d] Analyses of 7/77 and 5/78 series performed by LFE Laboratories, Richmond, California.

[e] N.D. = not detected.

[f] Trench 33L-4 sample collected 5/78 contained 8.8 E0 (22) pCi/L ^{22}Na.

Table 2

Organic Compounds Identified in Water Samples From Maxey Flats, Kentucky, Disposal Site

Compound	Water Sample		
	Trench 19S	Trench 32	Well UB1
Acidic Fraction			
2-Methylpropionic acid	0.40		
2-Methylbutanoic acid	4.6		
3-Methylbutanoic acid	1.8		
Valeric acid	2.0		
Isobutyric acid		2.0	
2-Methylbutyric acid		13	0.84
3-Methylbutyric acid		5.8	
Pentanoic acid		4.7	
2-Methylpentanoic acid		4.0	0.73
3-Methylpentanoic acid	3.1	1.4	0.16
C_6 branched acids	0.35		
Phenol		1.2	0.31
Hexanoic acid	1.5	4.7	1.1
2-Methylhexanoic acid	1.5	3.2	0.74
Cresol (isomers)	2.9	4.2	0.77
2-Ethylhexanoic acid	5.6	8.8	1.6
C_8 branched acid	1.4		
Benzoic acid	0.22	1.9	0.40
Octanoic acid	0.36	1.3	0.38
Phenylacetic acid	0.56	3.4	0.44
Phenylpropionic acid	1.2	9.8	0.38
Phenylhexanoic acid	N.Q.[a]	N.Q.	N.Q
Toluic acid (isomers)			0.41
Neutral Fraction			
p-Dioxane	N.Q.	N.Q.	N.Q.
Methyl isobutyl ketone	0.56		
Toluene	2.9	7.0	2.7
Xylene (isomers)	N.Q.	0.48	.12
Cyclohexanol	2.9	0.24	
Dibutyl ketone	N.Q.		
Fenchone	0.03		
Triethyl phosphate	0.38		
Naphthalene	0.12	0.28	0.09
Tributyl phosphate	0.16	0.36	
α-Terpineol		0.49	0.16

[a] Not quantified.

Table 3

Analysis of Trench and Well Water Samples Taken From Maxey Flats, Kentucky (10/30-11/2/79) (mg/L)[a]

Dissolved Component	Trench 19S	Trench 27	Trench 32	Well UB-1A	T-2E	T-3W	T-4E	T-5
pH	6.7	5.9	5.6	6.4[b]	6.6[b]	6.8[b]	7.1[b]	7.5[b]
Eh (mV, NHE)	57	140	-29	c	270	c	c	c
Dissolved Oxygen	<0.1	0.15	<0.1	c	0.1	c	c	c
Specific Conductance (μmho/cm@25°C)	1800	18000	3500	c	4000	c	c	c
Temperature(°C)	16.0	18.0	16.0	c	14.5	c	c	c
Chloride	170	6200	510	360	1300	1200	150	2000
Nitrogen (NO_3^-)	0.12	0.75	0.08	0.50	0.39	0.51	<0.05	1.4
Nitrogen (NH_4^+)	37	68	75	<1	1.0	13	<1	<1
Phosphate	<1	<1	1.2	<1	<1	<1	<1	<1
Silica	15	19	29	19	8.7	7.7	7.5	0.7
Sulfate	d	d	d	1700/1800[e]	550/540[e]	1000/1000[e]	1500/1500[e]	1300/1300[e]
DOC	300	500	670	5.1	120	15	29	14
Calcium	42	740	42	180	380	440	600	610
Iron	59	1400	0.5	0.1	1.6	1.2	0.5	0.2
Magnesium	130	720	300	300	160	95	95	130
Manganese	0.19	190	0.34	<0.1	3.5	2.7	1.1	0.2
Potassium	27	100	160	12	35	26	17	32
Sodium	480	770	720	530	530	910	280	1200
Strontium	0.65	6.7	0.52	2.6	7.7	6.6	5.6	8.4
Gross Alpha[f]	6.3 E4 (1.2)	6.9 E4 (<1)	9.7 E4 (<1)	<3.7 E0	7.6 E1 (24)	3.9 E1 (56)	1.7 E1 (64)	3.6 E1 (67)
Gross Beta[f]	3.2 E4 (<1)	1.9 E5 (<1)	5.9 E5 (<1)	1.0 E2 (34)	3.5 E4 (<1)	5.8 E2 (7)	<3.4 E1	<3.4 E1
Tritium[f]	d	d	d	d	6.1 E8	3.7 E7	1.3 E6	3.2 E4
^{90}Sr[f]	d	d	d	d	1.9 E4 (10)	d	d	d
^{238}Pu[f]	7.1 E4 (6)	2.6 E4 (10)	3.6 E4 (10)	2.5 E1 (10)	6.8 E1 (10)	1.6 E2 (10)	2.2 E1 (10)	4.9 E0 (18)
$^{239,240}Pu$[f]	2.5 E2 (6)	2.4 E3 (10)	7.9 E2 (10)	3.4 E-1(100)	1.0 E0 (10)	1.7 E0 (34)	8.9 E-1(50)	2.5 E-1(100)

[a] Measurement given in mg/L, unless otherwise noted.

[b] Laboratory measurement.

[c] In-line measurement not made.

[d] Analyses not completed.

[e] Determined by: colorimetric procedure/ion-chromatography.

[f] Radiochemical unit = pCi/L. Number in ( ) = 2σ% counting uncertainty.

Table 4

Sorption Coefficients for Trench Water and Shale From
Maxey Flats, Kentucky, Disposal Site
(Soil and Water Pretreatment)

	K_d (mL/g)[a]			
	Soil Condition			
	Oxic		Anoxic	
	Soil Condition			
Radionuclide	Ultrasonic Disaggregation	Ground 100-200 Mesh Fraction	Ultrasonic Disaggregation	Ground 100-200 Mesh Fraction
^{152}Eu	450±30	480±120	420±20	1480±270
^{241}Am	1240±180	560±230	480±70	900±20
^{85}Sr	6.1±0.8	48±4	4±1	10.0±0.3
^{134}Cs	1430±80	1300±100	570±30	490±2.0
^{137}Cs	1210±60	1570±40	550±30	490±10
^{60}Co	9±2	6.9±8	5±1	11±2

Trench Water:	Maxey Flats, disposal site, Trench 27 (MF-157), collected anoxically May 1978
Shale:	Maxey Flats, disposal site, Trench 46 (MF-III), unweathered shale at ~ 7 meters
Solution/Soil Ratio:	20 mL/g
Reaction Containers:	Screw cap, septum sealed, glass test tubes, Appendix F, Figure F.7 (Weiss, et al., 1980)
Equilibration Time:	100 hours
Anoxic:	Original materials maintained in an argon atmosphere
Oxic:	Trench water was exposed to air to precipitate ferric hydroxide. Samples were prepared from the solution after the precipitate was removed by filtration.

[a] K_d is reported as an average ± one standard deviation of the observed results.