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GEOCHEMICAL INVESTIGATIONS AT MAXEY FLATS RADIOACTIVE WASTE DISPOSAL SITE

TOPICAL REPORT

R. Dayal, R.F. Pietrzak, and J. Clinton

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ABSTRACT

As part of the NRC efforts to develop a data base on source term characteristics for low level wastes, Brookhaven National Laboratory (BNL) has produced and analyzed a large amount of data on trench leachate chemistry at existing shallow land burial sites. In this report, we present the results of our investigations at the Maxey Flats, Kentucky disposal site. In particular, data on trench leachate chemistry are reviewed and discussed in terms of mechanisms and processes controlling the composition of trench solutes. Particular emphasis is placed on identifying both intra- and extra-trench factors and processes contributing to source term characteristics, modifications, and uncertainties.

BNL research on the Maxey Flats disposal site has provided important information not only on the source term characteristics and the factors contributing to uncertainties in the source term but also some generic insights into such geochemical processes and controls as the mechanics of leachate formation, microbial degradation and development of anoxia, organic complexation and radionuclide mobility, redox inversion and modification of the source term, solubility constraints on solute chemistry, mineral authigenesis, corrosion products and radionuclide scavenging, and the role of organic complexants in geochemical partitioning of radionuclides. A knowledge of such processes and controls affecting the geochemical cycling of radionuclides as well as an understanding of the important factors that contribute to variability and uncertainties in the source term is essential for evaluating the performance of waste package and the site, making valid predictions of release for dose calculations, and for planning site performance monitoring as well as remedial actions.

The problems associated with unsegregated, poorly packaged, and unstabilized wastes encountered at the Maxey Flats disposal site point to the need for waste segregation, improved stabilization, and proper packaging. Stabilized, packaged waste not only ensures trench stability but also decreases the rate and extent of leaching and microbial degradation of buried waste. In addition, the uncertainties in the source term are reduced.

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EXECUTIVE SUMMARY

As part of the NRC efforts to develop a data base on source term characteristics for low level wastes, Brookhaven National Laboratory (BNL) has been involved in source term investigations at the commercially operated shallow land burial sites located in the eastern United States (Barnwell, South Carolina; Maxey Flats, Kentucky; Sheffield, Illinois; and West Valley, New York). The BNL research effort, during the past several years, has generated a large amount of data on source term characteristics and geochemical controls on trench leachate chemistry at existing shallow land burial sites. Current disposal procedures are much improved from those practised in the past, but several of the factors, conditions, and processes observed by BNL at these sites may be expected to occur at future shallow land burial sites.

BNL research on the Maxey Flats disposal site has provided some generic insights into such geochemical processes and controls as the mechanics of leachate formation, microbial degradation and development of anoxia, organic complexation and radionuclide mobility, redox inversion and modification of the source term, solubility constraints on solute chemistry, mineral authigenesis, corrosion products and radionuclide scavenging, and the role of organic complexants in geochemical partitioning of radionuclides. A knowledge of such processes and controls affecting the geochemical cycling of radionuclides as well as an understanding of the important factors that contribute to variability and uncertainties in the source term is essential for evaluating the performance of waste package and the site, making valid predictions of release for dose calculations, and for planning site performance monitoring as well as remedial actions.

In this report, we present the results of our investigations at the Maxey Flats disposal site. In particular, data on trench leachate chemistry are reviewed and discussed in terms of mechanisms and processes controlling the composition of trench solutes. Particular emphasis is placed on identifying both intra- and extra-trench factors and processes contributing to source term characteristics, modifications, and uncertainties.

A combination of hydrological and biogeochemical factors determine to a large extent the formation and compositions of trench leachates. At the Maxey Flats site, the waste trenches are located in non-porous, fractured shale of low hydraulic conductivity. This results in accumulation of rainwater that infiltrates through the trench caps. Such accumulation of stagnant water and its eventual overflow, which has been termed the "Bathtub Effect," has been observed in the Maxey Flats trenches. Because of the long residence time of accumulated water in the trenches, prolonged leaching and microbial degradation of buried waste material occurs continuously and leads to leachate formation. As a result of such interactions for extended time periods, the resultant trench leachates acquire geochemical properties which are unique, compared to ambient groundwater. Relative to ambient groundwater, the Maxey Flats leachates exhibit significant modifications in terms of inorganic, organic, and radionuclide solute constituents, attributable primarily to microbial degradation and leaching of buried waste materials.

The development of anoxia in trench leachates is largely controlled by microbial degradation of organic matter present in the buried wastes. A large fraction of wastes buried in the trenches consists of unconsolidated organic materials. Many components of these materials are subject to both aerobic and anaerobic microbial degradation processes. The anoxic conditions observed in the trench leachates are characterized by negative redox potentials, low dissolved oxygen and sulphate concentrations, the presence of dissolved sulphide, and high contents of alkalinity and ammonia, reflecting the nature and intensity of the microbial processes. An evaluation of redox equilibria and redox buffering in trench leachates indicates that Fe_2O_3/Fe^{2+} and $SO_4{}^{2-}/H_2S$ couples appear to be the dominant buffers controlling the redox conditions in most trench leachates.

The enrichments, to varying degrees, of inorganic, organic, and radionuclide constituents associated with fuel cycle and non-fuel cycle low-level wastes reflect the nature of the leaching process itself and of the waste materials. Elevated concentrations of Na^+, K^+, Fe_{total}, Mn_{total}, Cl^-, dissolved organic and inorganic carbon and several organic compounds, as well as radionuclides such as H-3, Am-241, Co-60, Cs-134, Cs-137, Sr-90, Pu-238, and Pu-239,240 are a consequence of waste leaching. Some of the waste-derived organic compounds present in the trenches such as chelating agents and several carboxylic acids are strong complexing agents and have the potential to form stable radionuclide complexes and thus enhance nuclide mobility.

In Maxey Flats trench leachates, representing relatively stagnant systems, where the products of waste leaching and microbial degradation are continually generated and subsequently accumulate, the leachate solutes are also subject to abiogenic precipitation reactions. The WATEQF geochemical code used to calculate saturation states of trench leachates with respect to several mineral phases indicate calcite, dolomite, and rhodochrosite are likely to form and exert control on the concentrations of Ca^{2+}, Mg^{2+}, Mn^{2+}, and $CO_3{}^{2-}$. In the case of iron equilibria, gross supersaturations are found with respect to siderite, mackinawite, amorphous FeS and pyrite. Some leachates, however, exhibit saturation with respect to vivianite, indicating that the Fe^{2+} and $PO_4{}^{3-}$ concentrations are most likely controlled by this mineral phase.

Laboratory oxidation experiments, performed to obtain generic information on the behavior of anoxic trench leachates as they encounter a less reducing environment along groundwater flow paths, demonstrated that, upon oxidation, a series of chemical changes were initiated which results in a drastically different solute chemistry. The experiments further showed that, even though precipitation of ferric oxyhydroxide occurred in most cases, coprecipitation or scavenging of the radionuclides was minimal. These observations indicate that some of the radionuclides may have formed complexes with organic complexing agents sufficiently stable to withstand scavenging by authigenic ferric oxyhydroxide, which represents a geochemical discontinuity where iron-rich, anoxic waters encounter a more oxidizing environment.

Evaluation of the balance between the initial alkalinity of trench leachates and the acidity generated as a result of the ferrous iron oxidation reaction shows that the Maxey Flats leachates represent well-buffered systems and that the amount of acid generated is not appreciable to affect the balance between acidity and alkalinity. This is important considering that an acid leachate would not only affect the inorganic and radionuclide solute species but also have a significant effect on leachate-sediment interactions.

Solubility calculations indicate that, in addition to significant changes observed in solute chemistry upon oxidation, certain carbonate and oxide mineral phases may form and exert control on solute chemistry at geochemical interfaces, representing zones where iron-rich, anoxic waters mix with oxic groundwater. These authigenic minerals could also have a profound effect on the geochemical partitioning of radionuclides.

Radionuclide sorption experiments performed to evaluate the role of organic complexing agents in waste migration show that cobalt forms relatively strong complexes with EDTA and NTA and that these complexes persist in strongly reducing, anaerobic environments typical of burial trenches, where anoxic conditions develop. As a result of the formation of such stable complexes, Maxey Flats shale is not very effective in removing cobalt from solution. On the other hand, the sorption of cesium and strontium remains unaffected in the presence of added complexing agents, indicating little affinity for alkali metals towards complex formation. These observations, together with our findings of a lack of removal of radionuclides from solution by authigenic ferric oxyhydroxide in oxidized trench leachates containing complexing agents, indicate the important role organic complexants play in the geochemical partitioning and mobility of radionuclides.

In situ leachate migration experiments conducted in the vicinity of two burial trenches demonstrated that migration of inorganic, organic, and radionuclide constituents does indeed occur on the disposal site. The experimental trench facility experiments showed that migration of contaminants occurs by subsurface pathways both out of and into trench 27. Experiments conducted in the vicinity of trench 19s also indicate subsurface migration of radionuclides away from the trench boundary. Because of its non-reactive nature, tritium was found to be the most mobile, and cesium the least. The types and concentrations levels of organic and radionuclide contaminants observed in well waters UB1 and UB1-A also suggest on-site, subsurface migration of leachates, derived from neighboring trenches, in the general direction of the UB wells. In most cases, the observed subsurface leachate migration is believed to occur along the fractured lower sandstone marker bed, which represents the base of most trenches at the site. Because Na^+, Cl^-, and H-3 are enriched in the trench leachates, as a result of waste leaching, and because they are known to be non-reactive geochemically, they serve as excellent inert tracers for leachate migration, as evident from the observed concentration gradients in the vicinity of trench 27.

The problems associated with unsegregated, poorly packaged, and unstabilized wastes encountered at the Maxey Flats disposal site point to the need for waste segregation, improved stabilization, and proper packaging. Stabilized, packaged waste not only ensures trench stability but also decreases the rate and extent of leaching and microbial degradation of buried waste. In addition, the uncertainties in the source term are reduced.

1. INTRODUCTION

Modeling of low-level waste disposal sites is an important consideration in evaluating the capability of future sites to conform with 10 CFR 61. A reliable estimate of the source term is essential for evaluating the performance of a waste package and the site, making valid predictions of release for dose calculations, and for planning site performance monitoring as well as remedial action in the event of seepage at the site.

Studies of existing low level waste disposal sites provide a unique opportunity to investigate the behavior and fate of radioactive waste nuclides in a natural setting and to assess the suitabilty of similar sites for future disposal of low level radioactive wastes. In addition, such investigations provide valuable information on source terms under a range of hydrological and geochemical conditions, on site behavior and waste package performance. The effects of disposal of unsegragated, unstabilized, and poorly packaged waste on trench environment can also be estimated.

As part of the NRC efforts to develop a data base on source term characteristics, Brookhaven National Laboratory (BNL) has been involved in source term investigations at the commercially operated shallow land burial sites located in the eastern United States (Barnwell, South Carolina; Maxey Flats, Kentucky; Sheffield, Illinois; and West Valley, New York). The BNL research effort, during the past several years, has generated a considerable amount of data on source term characteristics and geochemical controls on trench leachate chemistry at existing shallow land burial sites. Although the current disposal procedures are much improved from those practiced in the past, it is highly likely that several of the factors, conditions, and processes observed by BNL at these sites can be expected to occur at future shallow land burial sites.

Although difficult to interpret quantitatively because of the heterogeneity and a lack of knowledge of the quantity and reactivity of the buried waste materials, BNL work, especially at the Maxey Flats disposal site, has provided some generic insights into such geochemical processes and controls as the mechanics of leachate formation, microbial degradation and development of anoxia, organic complexation and radionuclide mobility, redox inversion and modifications in the source term, corrosion products and radionuclide scavenging, and solubility constraints and mineral authigenesis. A knowledge of such factors, controls, and processes which characterize the source term and contribute to source term modifications is essential for obtaining a reliable estimate of the source term, an important consideration in evaluating the capability of future sites to conform with 10 CFR 61.

In this report, we present the results of our investigations at the Maxey Flats disposal site. In particular, data on trench leachate chemistry are reviewed and discussed in terms of mechanisms and processes controlling the composition of trench solutes. Particular emphasis is placed on identifying both intra- and extra-trench factors and processes contributing to source term characteristics and modifications.

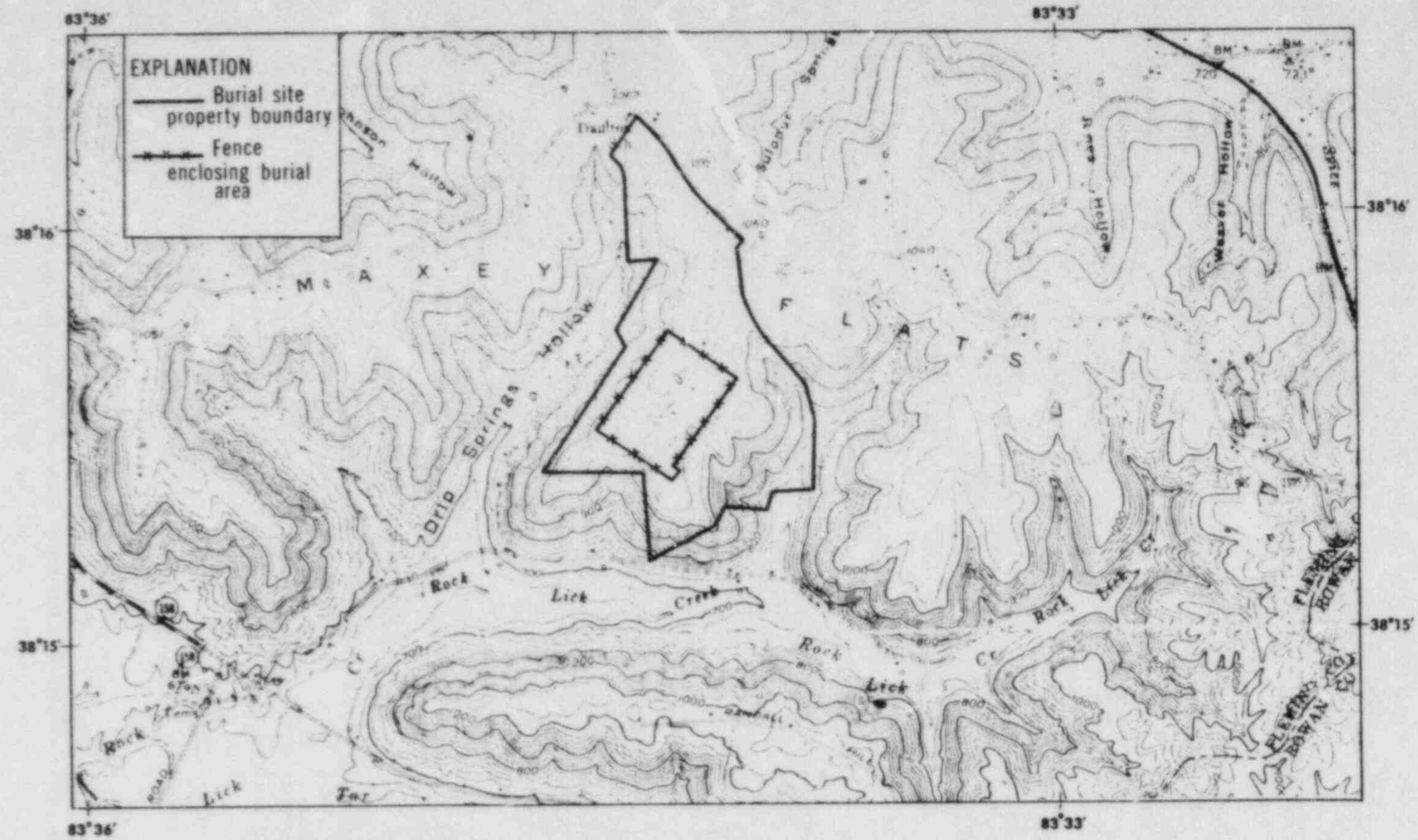
The main issues addressed in this report include:

- Which processes control leachate formation and development of anoxia in the trenches?
- What are the important solute constituents characteristic of trench leachates?
- What processes and couples determine redox equilibria and buffering in trench leachates?
- What are the important biogeochemical processes controlling leachate compositions?
- What are the solubility constraints on leachate composition?
- What is the potential role of waste-derived organic solutes on radionuclide partitioning and mobility?
- What are important constituents that serve as conservative tracers for leachate migration?
- What are the important extra-trench processes contributing to source term modifications? Does authigenic ferric oxyhydroxide act as an in situ scavenger for radionuclides and to what extent can radionuclide complexes withstand scavenging by authigenic minerals?
- Which solute constituents serve as tracers for in situ leaching and microbial degradation of buried wastes?
- The relevance of the findings of this study to NRC needs.

1.1 Site Characteristics and Hydrogeology

Detailed descriptions of site characteristics and hydrogeology have been reported by Zehner (1983) and Meyer (1976). Briefly, the burial site is located on Maxey Flats, an eroded plateau in the knobs region of northeastern Kentucky (Figure 1.1). The plateau rises approximately 300 to 400 feet above the surrounding alluvium-filled valley. The Maxey Flats region has a humid continental climate with sharp contrasts between winter and summer months. Based on the reported mean annual precipitation of 43 inches, the Maxey Flats site can be characterized as a humid site.

As shown in the diagrammatic geologic section of the Maxey Flats site (Figure 1.2), the burial trenches are excavated entirely in the Nancy Member of the Borden Formation. The upper 1 to 25 feet at the site is yellow brown regolith composed of weathered shale. McDowell et al. (1971) reported the presence of two sandstone beds of variable thickness (in feet) located at about the middle and at the base of the regolith. In some places, the shale between the two sandstone beds is partly weathered, imparting a mottled yellow



Base from U.S. Geological Survey Plummers Landing 1:24000, 1951, revisions as of 1979 and Farmers 1:24000, 1970.

CONTOUR INTERVAL 20 FEET

National Geodetic Vertical Datum of 1929

Figure 1.1. Location of the Maxey Flats waste disposal site (From Zehner, 1983).

brown and gray color to the rock unit. The unweathered part of the Nancy Member, which averages about 15 feet in thickness, extends from the base of the lower sandstone bed in the weathered part of Nancy shale and is underlain by a 1.5-foot thick sandstone bed, at a depth of approximately 25 feet.

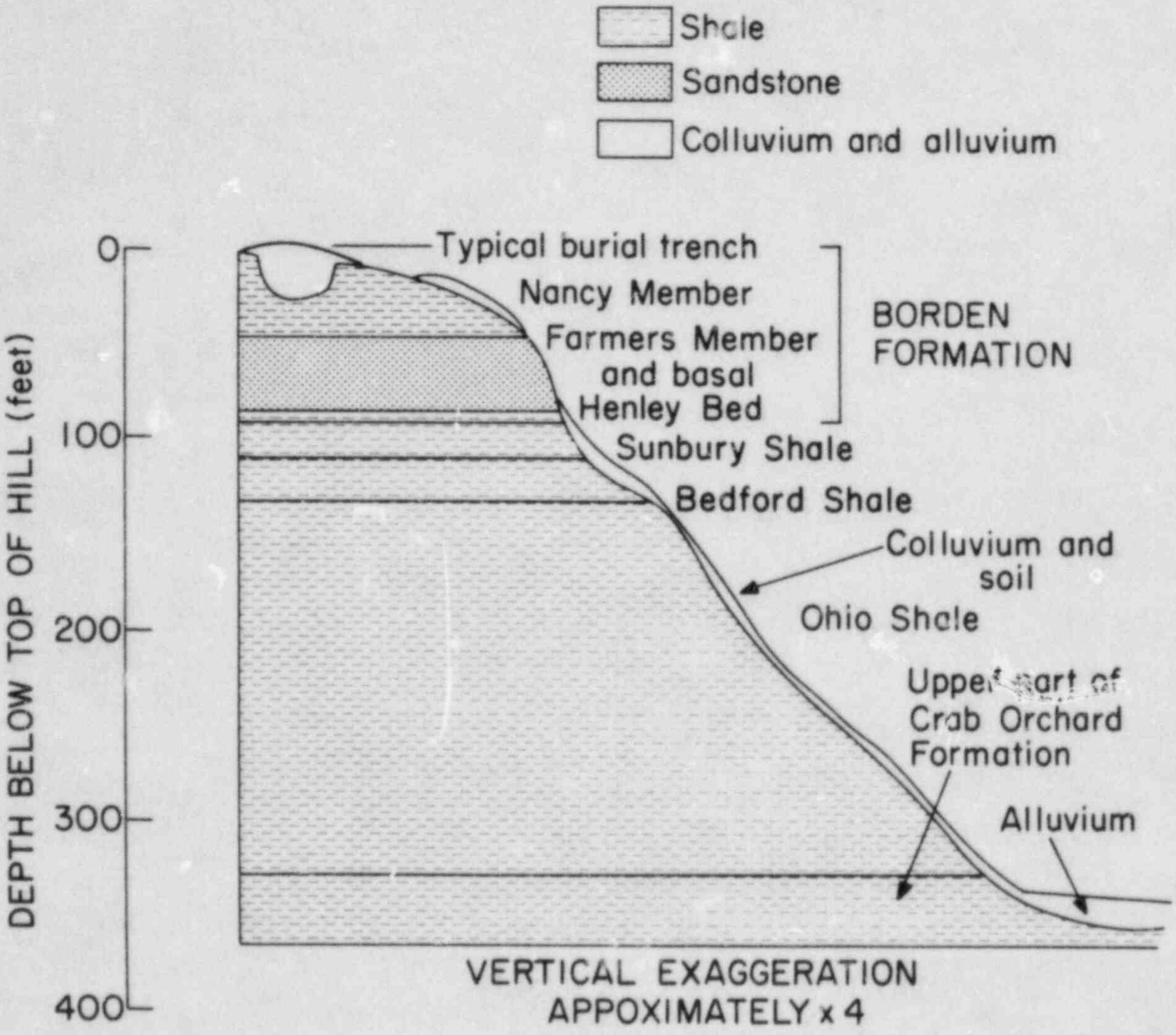


Figure 1.2. Diagrammatic geologic section of the Maxey Flats site (After Zehner, 1983).

About 80% of the rocks underlying the burial site are shale. Because of the extremely low hydraulic conductivity of the bedrock, virtually most groundwater movement occurs through fractures and joints. Saturated zones are present in the upper part of Nancy Member. The upper most water table is perched in the soil zone overlying the poorly permeable unweathered Nancy shale and supplies the shallow wells on Maxey Flats. According to Meyer (1976), almost all water discharging from the site and from the underlying subsurface formations is believed to originate from precipitation falling on the site. Zehner (1983) estimated the maximum potential discharge from bedrock in the drainage below the site to be 0.1 inch per year, which corresponds to about 5% of the mean annual base flow. The remaining 95% is reported to be groundwater discharge from colluvium and alluvium that cover valley slopes and bottoms.

1.2 Site Operations

The Maxey Flats site was operational from May 1963 until the end of 1977. By 1972, some of the completed trenches were filled or partially filled with infiltrating water. A water management program was initiated to remove the accumulated water in the trenches and to control further entry of water. Efforts towards water removal included pumping the water out of trenches, storing the leachates in a surface storage tank, reducing the leachate volume by evaporation, and solidification of evaporated residues for eventual disposal on site. Efforts to minimize water ingress included grading and improving surface drainage, recapping older trenches to reduce cap permeability, and establishing a vegetation cover over completed trenches (Mills and Page, 1982). A temporary remedial measure taken in 1981 to minimize entry of infiltrated water into the trenches involved installation of a 15 mL PVC plastic cover over the surface of trenches located in the middle and western sections of the burial area. As a short-term solution, the trench cover appears to be effective in preventing surface runoff from infiltrating into the trenches.

1.3 Waste Character, Inventory and Burial

Based on reports by Zehner (1983), Mills and Page (1982), Meyer (1976), Gat et al. (1976) and Clarke (1973), the following information has been gathered on the waste inventory of the site and on the character and volumes of wastes buried at the site.

During 1962-1977, the period of commercial operation, approximately 4.8 million cubic feet of waste comprising of 2.4 million curies of by-product material, 431 kilograms of special nuclear material, and 533,000 pounds of source material were buried at the site. As defined in 10CFR20, by-product material represents materials that become radioactive by neutron activation in reactors; special nuclear material consists of plutonium, U-233, and enriched U-235; and source material corresponds to uranium and thorium, but does not include special nuclear material.

Most of the wastes buried at Maxey Flats were in solid form and consisted of low activity wastes such as paper, trash, clothing, protective apparel, laboratory glassware, obsolete equipment, radiopharmaceuticals, and miscellaneous rubble. Higher activity wastes included solidified liquids, shielding accessories, filter cartridges, ion-exchange resins, and activated metals. Transuranic wastes are generally associated with glove boxes, rubber tubing, gaskets, plastics, paper and rags.

Most solid wastes were contained in 55-gallon steel drums, especially the more hazardous materials. The less hazardous wastes were generally packaged in fiberboard boxes or wooden crates. During the early years of operations, burial of container-enclosed liquids and solidified liquid wastes is also reported to have occurred (Zehner, 1983). The packaged solid wastes were dumped at random in large rectangular trenches separated by 5 to 10 feet of shale and covered by 3 to 10 feet of compacted clay admixed with crushed shale. Many packages were crushed from the impact of dumping or during compaction of the trench cap.

Most trenches are about 300 feet long, 25 feet wide, and 20 to 25 feet deep. The bottoms are slightly sloping to facilitate collection of infiltrating water accumulated at the bottom of the riser pipes. Most trenches contain one or two steel riser pipes, which are used for routine observation of water levels and for removal of trench water.

Zehner (1983) reported that "s" trenches, such as 5s and 19s, were used for burial of "special" types or amounts of wastes having relatively long biological or radioactive half-lives (Sr-90, Plutonium). Solidified liquid wastes, or liquid holding tanks, were buried in "L" trenches. Most "L" trenches are much smaller than the common trenches. Trench 33L consists of several adjacent slit trenches, ranging in width from 2 to 8 feet. The slit trenches, about 250 feet long and 10 feet deep, were lined with plastic and filled with liquid waste slurries, which eventually solidified. For example, cement and urea formaldehyde were used as solidification agents in slit trenches 33L4, 33L11, 33L16 and 33L17, and 33L3 and 33L18, respectively.

Some trenches have one or more riser pipes for water removal. The riser pipes are identified by a number or letter following the trench number. Trench 34 has four riser pipes, trench 31 has risers in its east and west ends, and trenches 40, 43, and 44 have risers in the north and south ends. The 33L slit trenches have one or more riser pipes.

As compiled by Zehner (1983), approximate trench dimensions and their closure dates, waste volumes and the amount of radioactivity at the time of burial in each disposal trench at the site are shown in Table 1.1. The levels of radioactivity of liquid wastes are also included in the Table. For the purposes of this study, it should be noted that trench 2 was closed in 1963 and trenches 40 to 45 in the mid seventies.

Table 1.1. Trench dimensions, closure dates, and waste characteristics.[a]

Trench	Trench Dimensions[b] (ft)	Trench Volume (ft^3)	Solid waste Volume (ft^3)	Radioactivity at Time of Burial (curies)	Date Closed (month/year)
1	150-10-15	22000	7	306	5/63
1s	75-25-15	28000	580	2300	9/63
2	180-25-15	68000	c	c	7/63
3	250-25-15	56000	500	5900	9/63
4L	30-15-15	6800	0	1	10/63
5s	30-15-14	6300[d]	7800[d]	6480	4/64
6L	25-15-14	5200	1000	<1	11/63
7	225-15-15	50000	23000	16200	4/64
8L	20-15-13	3900	0	<1	1/64
9L	20-15-12	3600	c	c	3/64
10	300-30-15	140000	78000	426000	12/64
11s	300-30-12	100000	45000	16100	9/65
12L	15-10-08	1200	84	2	7/64
13L	15-10-08	1200	56	<1	9/64
14L	15-09-05	700	c	c	6/66
15	300-50-12	180000	73000	44900	9/65
16L	15-10-08	1200	3	<1	4/65
17L	30-15-10	4500	0	5	12/65
18	300-40-09	100000	75000	49100	2/66
19s	300-40-10	120000	69000	66800	12/66
20	300-40-12	140000	77000	103000	11/66
21L	300-42-15	190000	25000	2540	c
22	300-20-12	72000	3000	20600	1/72
23	300-60-10	180000	60000	20400	6/67
24	300-50-10	150000	62000	8420	10/67
25	300-30-11	99000	49000	18100	1/68
26	300-50-10	150000	66000	11000	5/68
27	350-70-18	440000	160000	35200	2/69
28	350-70-18	440000	160000	34700	9/69
29	350-70-18	440000	240000	871000	6/70
30	460-75-22	760000	240000	30600	2/71
31	460-75-22	760000	190000	672000	10/71
33L	c	c	0	809	1/72
34	500-30-10	150000	900	79100	8/72
35	300-70-20	420000	67000	13900	10/72
36	200-20-18	72000	14000	5670	11/72
37	200-20-18	72000	15000	1370	12/72
38	200-20-17	68000	19000	222	12/72
39	200-50-16	160000	27000	36	7/73
32	350-70-22	540000	120000	27000	5/72
40	868-70-30	1400000	440000	c	5/74
41	c	c	c	c	1/73
42	650-70-30	1400000	370000	c	6/75
43	614-50-30	920000	390000	c	12/75
44	681-55-30	1100000	500000	c	9/76
45	c	c	55000	c	11/77

[a] Data from Kentucky Department for Human Resources as compiled by Zehner (1983).

[b] In order of length, width, and depth.

[c] Data not available.

[d] Data probably in error because volume of waste exceeds volume of trench.

Table 1.2 shows a compilation of initial radioactivity in each trench expressed as ratios of radioactivity to waste volume and trench volume. The ratio of waste volume to trench volume is also presented in Table 1.2 to give an indication of the magnitude of void space in each trench. In most cases, more than 50% of the trench volume represented void spaces at time of burial. Only in trenches 10, 19s, and 20, the void space appears to be less than 50% of the trench volume. Zehner (1983) reported further that the overall void space in a trench has probably decreased since the time of burial due to compaction of the waste by heavy equipment during burial and trench capping, settling of the waste by itself, microbial degradation and leaching of waste with time. In addition, container failure at the time of burial probably also contributed to compaction of packaged waste, thus resulting in an increase in void space. The observed subsidence of trench caps in recent years is a result of trench instability attributable to increase in void space with time. The occurrence of subsidence holes on the trench caps indicate a net decrease in void space in the trenches (Zehner, 1983).

Table 1.2. Concentration of radioactivity in waste and waste trenches.[a,b]

Trench	Ratio of Radioactivity to Waste Volume (curies/ft^3)	Ratio of Radioactivity to Trench Volume (curies/ft^3)	Ratio of Waste Volume to Trench Volume	Void Space in Trench (%)
1	44	0.01	<0.01	>99
1s	4.0	0.08	0.02	98
3	12	0.11	0.01	99
7	0.70	0.32	0.46	54
10	5.4	3.0	0.56	44
11s	0.36	0.16	0.45	55
15	0.61	0.25	0.41	59
18	0.70	0.50	0.80	20
19s	0.97	0.56	0.58	42
20	1.3	0.74	0.55	45
22	6.9	0.29	0.04	96
23	0.34	0.11	0.33	67
24	0.14	0.06	0.41	59
25	0.37	0.18	0.49	51
26	0.17	0.07	0.44	56
27	0.22	0.08	0.36	64
28	0.22	0.08	0.36	64
29	3.6	1.9	0.55	45
30	0.13	0.04	0.32	68
31	3.5	0.88	0.25	75
32	0.22	0.05	0.22	78
35	0.21	0.03	0.16	84
36	0.40	0.08	0.19	81
37	0.09	0.02	0.21	79
38	0.01	0.003	0.28	72
39	<0.01	<0.001	0.17	83
40	c	c	0.31	69
42	c	c	0.26	74
43	c	c	0.42	58
44	c	c	0.45	55

[a] Values calculated from data in Table 1.1 by Zehner (1983).

[b] Radioactivity at time of burial.

[c] Data not available.

1.4 Research Investigations at Maxey Flats

In a chronological review of NRC research investigations at the Maxey Flats low-level waste disposal site, O'Donnell (1983) reported that NRC funded research at Maxey Flats began in the mid 1970's when BNL undertook an investigation of the source terms at commercially operated shallow land burial sites [Barnwell (South Carolina), Maxey Flats (Kentucky), Sheffield (Illinois), and West Valley (New York)] located in the eastern United States. At about the same time, Los Alamos National Laboratory (LANL) collected soil samples at the Maxey Flats site for an investigation of soil-radionuclide interactions. In response to reports of localized movement of Co-60 and Mn-54 within the site boundary and the detection of measurable amounts of other radionuclides in the colluvium on the hillslopes of the disposal facility and in streams bordering these slopes, NRC's Office of Nuclear Regulatory Research formulated a research program to assist the State of Kentucky, an Agreement State.

Areas of research in the overall NRC program have included water entry into burial trenches, characteristics of the trench leachates, geochemical controls on trench leachate compositions, leachate-soil interactions, chemical species of migrating radionuclides and the role of organics in radionuclide migration, the use of vegetation for detection of radionuclide contamination, and in situ leachate migration studies. During the past several years, the NRC research program has generated site specific information which can be used by the State of Kentucky in its assessment of site performance as well as for developing a plan for eventual site closure. In addition, the research program has provided generic data on the migration behavior of radionuclides under chemically reducing conditions, leachate-soil interactions in the presence of organic chelating agents, the effects of such processes as microbial degradation and leaching of buried waste on trench leachate compositions, and the effects of disposal of unsegregated and unstabilized wastes on trench environment.

The participating organizations and their specific involvement in the NRC sponsored research program on Maxey Flats disposal site as summarized by O'Donnell (1983) are listed below:

Brookhaven National Laboratory--Characterization of trench leachate chemistry and identification of processes controlling leachate compositions (Dayal et al., 1984; Pietrzak et al., 1982; Czyscinski and Weiss, 1981; Weiss and Colombo, 1980).

Commonwealth of Kentucky--Preliminary investigations at Maxey Flats disposal site (Clark, 1973).

Geo-Centers, Inc.--Assessment of ground penetrating radar for detecting shallow land burial trenches.

Laboratory of Nuclear Medicine, University of California, Los Angeles--Assessment of the characteristics of radionuclides and soils which govern uptake by plants (Wallace et al., 1980; 1979).

Los Alamos National Laboratory (LANL)--Assessment of the effect of the soils at Maxey Flats on radionuclide migration (Polzer et al., 1984; 1982).

Pacific Northwest Laboratory (PNL)--Investigation of the chemical species of migrating radionuclides at Maxey Flats (Kirby et al., 1984; 1982) and of the use of vegetation for detecting releases of radioactivity at shallow land burial facilities (Rickard et al., 1982).

University of California, Berkeley (UCB)--Investigation of water entry into burial trenches and its management by agronomic means (Schulz, 1984; 1982).

University of Arizona (UA)--Recent investigations of the use of organic tracers to determine water flow directions between burial trenches and an assessment of alternative methods of ensuring trench cap stability (McCray, 1983). In 1980 a similar experiment was conducted by Nowatzki et al. (1981) at Maxey Flats.

Other organizations that have been involved in research at Maxey Flats include the State of Kentucky, Contractors to the State, the U. S. Environmental Protection Agency, and the U. S. Geological Survey. The findings of these investigations are summarized in Zehner (1983),Mills and Page (1982), Cleveland and Rees (1981), Clancy et al. (1981), and Meyer (1976).

1.4.1 Experimental Areas at Maxey Flats Disposal Site

Two experimental facilities were established at Maxey Flats to investigate in the field the movement of water and radionuclides in the vicinity of burial trenches as well as the performance of the trench caps (Figure 1.3).

A series of five experimental trench sections were constructed at the southwest corner of the burial site in 1979 for the purpose of intercepting groundwater flow paths in the vicinity of disposal trench 27. In 1980, inert atmosphere wells were installed near the experimental trench sections to prevent oxidation of water samples during collection. UA, UCB, BNL, LANL, and PNL used the facility jointly and cooperated in the experiments.

Another experimental facility was established in the vicinity of burial trench 19s (Figure 1.3). A large number of porous caps and soil moisture sensors were installed to sample intersitial water and to measure soil water content periodically. UCB, BNL, and LANL used this facility for soil moisture and radionuclide migration studies.

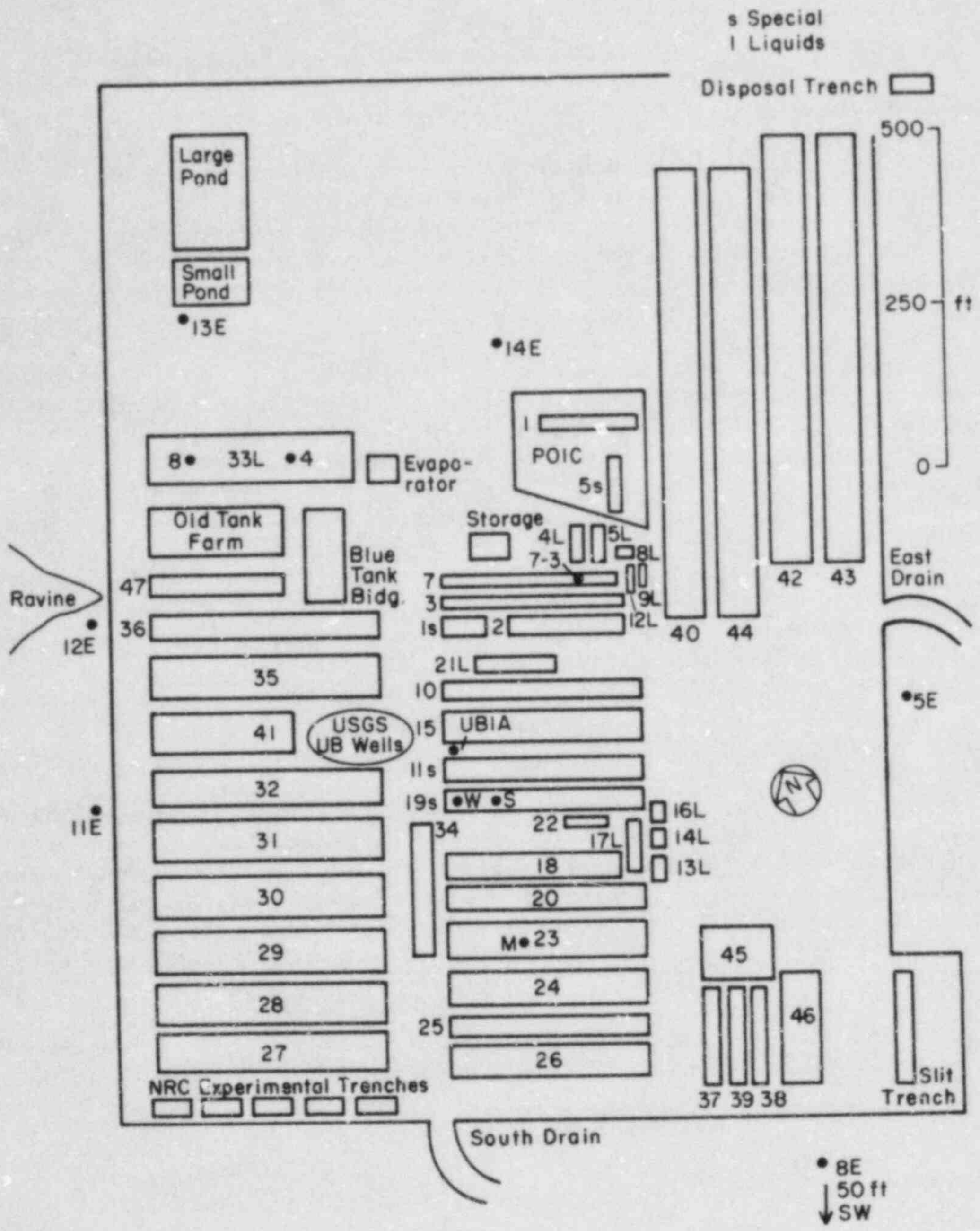


Figure 1.3. Schematic of the Maxey Flats site, showing the location and identification of the disposal trenches. The exact location of the sump standpipes in the trenches is also shown as M in trench 23, W and S in trench 19s, 7-3 in trench 7, and 4 and 8 in trench 33L. The experimental trench sections are shown in the southwest corner of the disposal site. The other experimental facility was established between trenches 19s and 18 (From Kirby et al., 1984).

1.4.2 Description of Maxey Flats Research at BNL

A major part of the source term investigations by BNL at the Maxey Flats disposal site involved analyses and characterization of water samples collected from disposal trenches and from on- and off-site wells (Dayal et al., 1984; Czyscinski and Weiss, 1981; Weiss and Colombo, 1980). In addition to sampling trench leachates and well waters, water samples were also taken from a series of experimental trench sections.

Radionuclide sorption studies involved batch and column laboratory experiments using Maxey Flats leachate and shale samples and performed under conditions simulating the trench environments (Pietrzak et al., 1982; Czyscinski and Weiss, 1981; Weiss and Colombo, 1980). Of particular interest was to determine the effect of selected organic complexing agents on radionuclide sorption. A series of gel-filtration chromatography experiments were also performed on selected trench leachates to determine the presence and nature of organo-radionuclide complexes.

The BNL effort also included a microbiological study to enumerate the abundance and distribution of microorganisms active in the trench leachates and to evaluate the effects of various microbial processes on the transformation and migration of the buried radionuclides from the trenches (Francis, 1982; Francis et al., 1980).

Laboratory oxidation experiments were performed on several trench leachates to evaluate the behavior of iron- and organic-rich, anoxic trench leachates as they encounter a chemically less reducing environment along the groundwater flow paths. Particular emphasis was placed on radionuclide scavenging by authigenic ferric oxyhydroxide which represents a geochemical discontinuity where anoxic waters encounter an oxidizing environment (Dayal et al., 1984).

A detailed chronology of the various sampling trips undertaken by BNL to the Maxey Flats disposal site during the period 1976-1981 is given below:

1.4.3 Chronology of BNL Sampling Trips to Maxey Flats

Preliminary Study

Water samples were initially obtained from the Maxey Flats disposal site in April 1976 to gain experience in the collection, handling, and analyses of trench and well waters. The water samples, during this sampling trip, were collected jointly with the U. S. Geological Survey (USGS), State of Kentucky, and with the assistance of Nuclear Engineering Company (NECO) personnel at the site.

A series of trenches and two off-site wells were sampled (Weiss and Colombo, 1980). Field measurements and sample filtration were performed on the site, in a laboratory provided by NECO, within an hour after sample collection.

Weiss and Colombo (1980) reported that the initially clear trench leachates became cloudy with the formation of a reddish-brown iron hydroxide precipitate upon exposure to air. The iron that precipitated from the leachates and was subsequently filtered from the samples contained material that was originally dissolved in the water. Radionuclides and other solutes that were originally in solutions in the trench environment may have been adsorbed onto, or coprecipitated with, the iron hydroxide. Therefore, the results of these analyses do not reflect the actual trench leachate compositions.

Procedures were developed to prevent air from coming in contact with trench water samples during collection and filtration. These procedures were employed to collect water samples during subsequent sampling trips to Maxey Flats.

1976 Sampling

In September 1976, a series of trenches were sampled at the disposal site using the anoxic sampling procedures developed at BNL. As discussed above, previous sampling for the preliminary study was conducted under aerobic conditions which resulted in ferric hydroxide precipitation. Therefore, precautions were taken to collect samples under anoxic conditions in accordance with procedures developed for this purpose.

Leachate samples were collected from trenches 2, 7, 18, 19s, 26, 27, 32, 33L4, 33L9, and 37. Field measurements were made for pH, temperature, and specific conductance. The filtered leachate samples were subsequently analyzed for dissolved inorganic, organic, and radiochemical constituents using procedures described elsewhere (Weiss and Colombo, 1980).

1977 Survey Study

In order to select specific trenches for detailed investigations, a survey study was conducted during the summer of 1977. A total of 46 trenches and 5 on-site wells were sampled as part of this survey. USGS personnel, conducting hydrogeological studies at the disposal site, collected the water samples for the survey study. Samples were obtained from most trenches and wells that contained accumulated water at the time of sampling. Surface and groundwater samples were also collected from areas adjacent to the disposal site (Weiss and Colombo, 1980).

All disposal trenches (from trench 1 to trench 44s), except 12L, 13L, 28, 29, 33L2, 33L5, 33L7, 33L14, 33L15, 34-2, 34-3, 40s, 41, 43N, and 43s, were sampled. In addition, ten water samples from off-site wells and streams in the vicinity of the burial site were collected.

Field measurements were made for temperature, specific conductance, and pH. The water samples were analyzed for dissolved radionuclides and dissolved organic carbon, but analysis of other constituents was not conducted.

1977 Sampling

Following the survey study in June 1977, a sampling trip was planned a month later in July 1977 to collect water samples from trenches 2, 26, and 32. The leachates were analyzed for inorganic, organic, and radiochemical constituents. Field measurements included pH, Eh, temperature, and specific conductance.

1978 Sampling

In May 1978, several trenches and an on-site well were sampled. Specifically, water samples from trench 19s, 27, 33L4, 33L18, and well UB1A were collected. The water samples were analyzed for inorganic, organic and radiochemical constituents. Field measurements were made for pH, Eh, dissolved oxygen, temperature, and specific conductance. In addition, radionuclides in suspended particulates present in trench and well waters were determined.

1979 Sampling

Four disposal trenches were sampled along with one observation well and five experimental trench sections in October 1979. Anaerobic sampling procedures were used for the disposal trenches and one of the experimental trench sections (2E). The other experimental trench sections did not contain sufficient accumulated water for the anaerobic sampling system to be used. Among the disposal trenches sampled were 19s, 27, 30, and 32. The experimental trench sections included T2E, T3W, T4E, and T5. The on-site well sampled was UB1A. Field measurements were made for pH, Eh, specific conductance, dissolved oxygen and sulphide, and temperature. The leachates were analyzed for inorganic, organic, and radiochemical constituents.

1981 Sampling

During October 1981, seven disposal trenches were sampled using anaerobic procedures. In-line measurements of temperature, specific conductance, dissolved oxygen, sulphide, Eh, and pH were also performed using methods reported previously (Czyscinski and Weiss, 1981; Weiss and Colombo, 1980). The analyses of leachates collected from trenches 7, 19s, 23, 27, 33L4, 33L8, and 35 included inorganic and radiochemical constituents. The analysis of organic constituents included primarily chelating agents.

2. WATER SAMPLING AND ANALYSIS

The following is a summary of the field sampling and laboratory procedures that were developed at BNL and employed for the collection, storage and analysis of trench and well water samples from the low-level radioactive waste disposal sites. Further details of these procedures can be found in Pietrzak et al. (1982), Czyscinski and Weiss (1981), and Weiss and Colombo (1980).

2.1 Sampling Methods and Analytical Procedures

Procedures were developed to maintain the anoxic character of the trench waters during sampling. A schematic diagram of the anoxic water sampling system is shown in Figure 2.1. After collection, the water samples were stored in 4-liter borosilicate glass bottles designed to maintain the trench redox conditions. The anoxic collection procedure allows samples to be stored for months without oxidation, which results in a reddish-brown ferric hydroxide. A scheme for sequential processing of water samples collected in the field and subsequent analysis for the various dissolved and suspended constituents is shown in Figure 2.2.

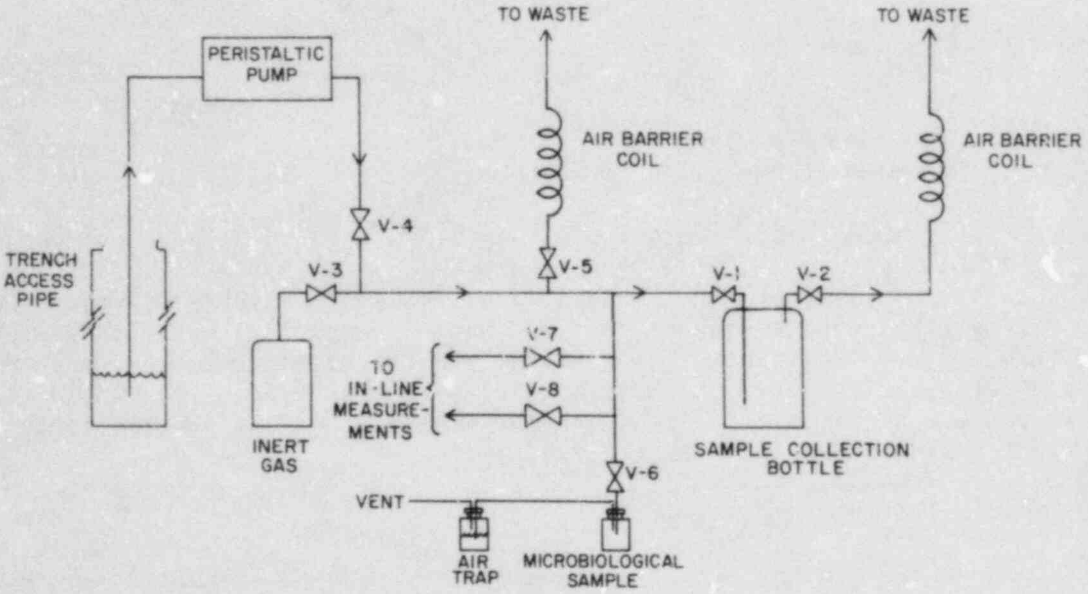


Figure 2.1. Schematic of the anoxic water sampling system.

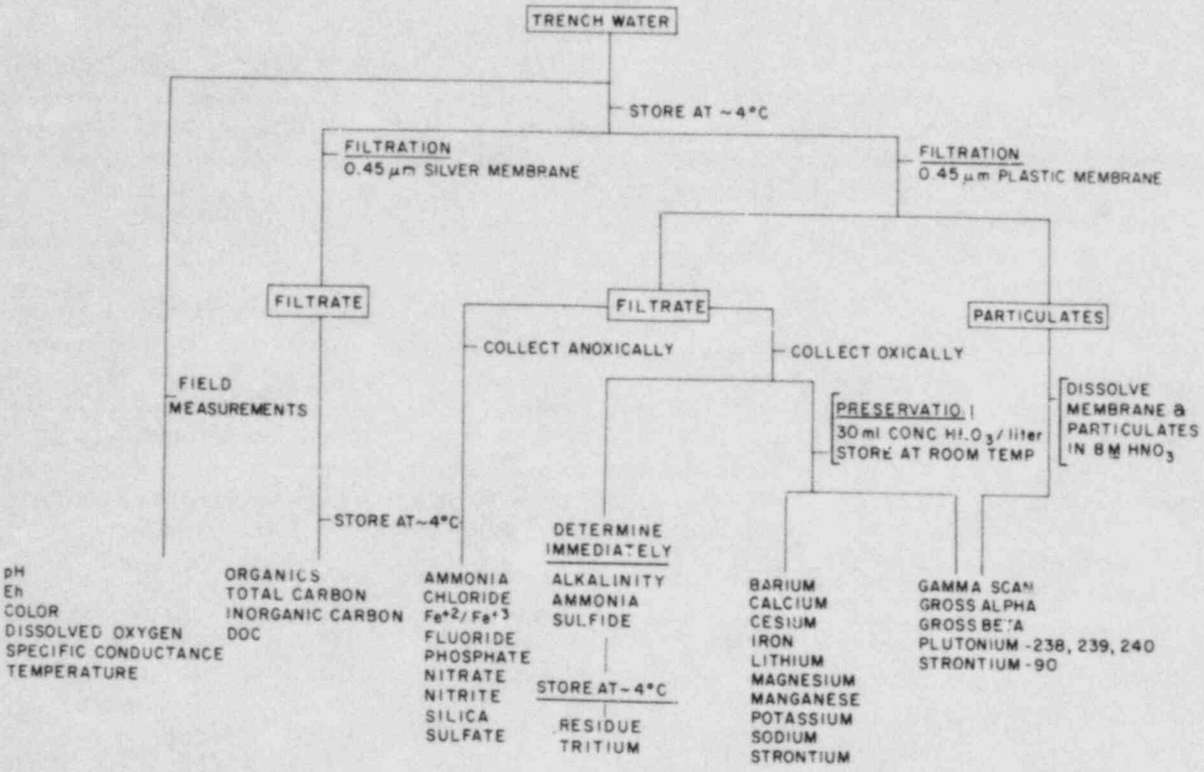


Figure 2.2. Scheme for sequential processing of water samples for analysis.

2.1.1. In-line Field Measurements

Physico-chemical characteristics of trench water which are subject to change during storage were measured at the time of sample collection. The temperature, pH, redox potential (Eh), dissolved oxygen and sulphide, and specific conductance of the trench water samples were measured in-line while the water sample was being collected. A schematic diagram of the in-line field measurement system is shown in Figure 2.3.

2.1.2 Anoxic Filtration

Upon arrival at BNL, the trench water samples were filtered through 0.45 μm membrane filters to remove suspended particulate matter. The filtration was also conducted under an inert atmosphere to maintain the anoxic character of the waters. The filtrate was divided into several fractions and processed according to the scheme shown in Figure 2.2. The dissolved fraction of each sample was analyzed for inorganic, organic, and radiochemical constituents. The particulate fraction was analyzed for radiochemical constituents only. A schematic diagram of the anoxic filtration system is shown in Figure 2.4.

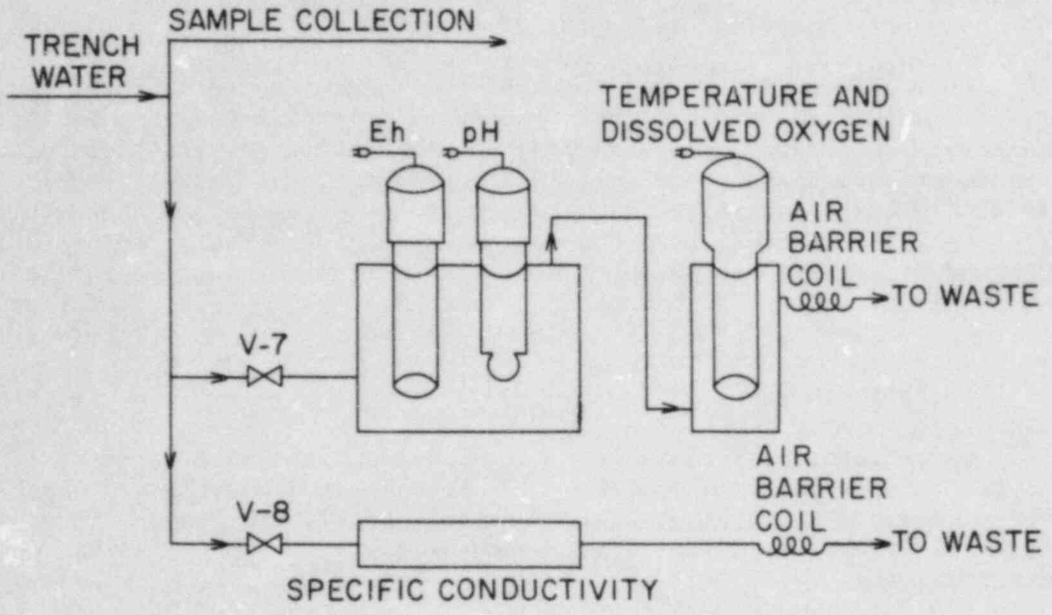


Figure 2.3. Schematic of the in-line field measurement system.

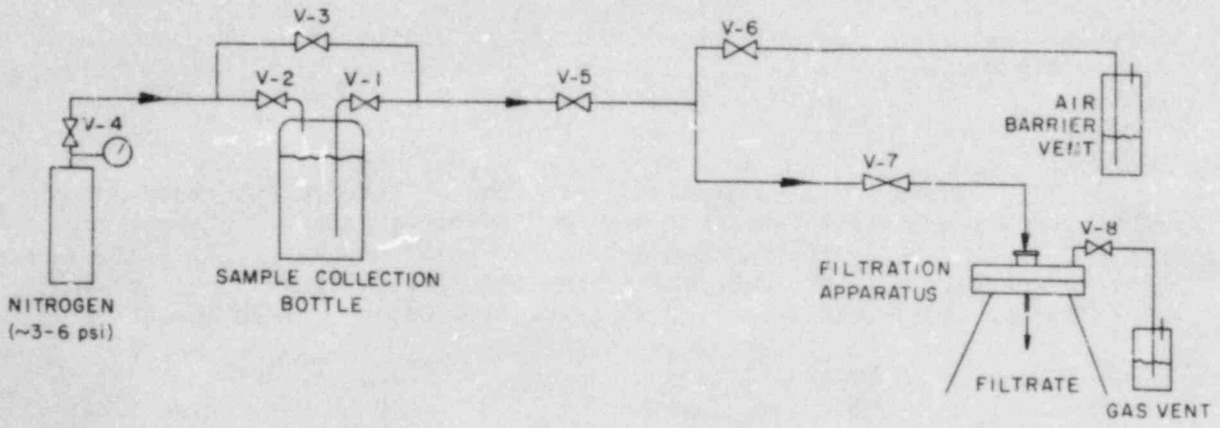


Figure 2.4. Schematic of the anoxic filtration system.

2.1.3 Inorganic Constituents

The following is a brief summary of methods used to measure the dissolved chemical constituents in trench waters sampled prior to 1981. Trench waters collected during the 1981 sampling trip were analyzed for inorganic constituents at BNL using ion chromatographic methods. Specifically, the anions chloride, sulphate, nitrate, phosphate, fluoride, and bromide were analyzed on a Dionex Model 10 ion chromatograph using an anion column with a 0.002 M sodium bicarbonate, 0.002 M sodium carbonate buffering solution. Ions were detected by changes in the electrical conductivity of the buffering solution.

2.1.3.1. Alkalinity

The alkalinity titration was performed on filtered trench water, immediately after filtration. Generally carbonate and bicarbonate concentrations in groundwater are determined by titrating the water sample with a standard acid to pH 8.3 and pH 4.5, respectively. The equations that govern the reactions are

$$CO_3^{2-} + H^+ \rightleftarrows HCO_3^- \qquad (2.1)$$

$$HCO_3^- + H^+ \rightleftarrows H_2O + CO_2 \qquad (2.2)$$

The end points of these titrations are usually sharp in the absence of other ions that are in competition for the hydrogen ion. In the presence of salts of weak organic and inorganic acids the titration curve does not give a sharp endpoint due to buffering of the system. The titration alkalinity in this case is not a simple function of the carbonate-bicarbonate concentrations. However, for the sake of simplicity, we have assumed the titration alkalinity to be equal to carbonate alkalinity. The shape of an acid-base titration curve can yield useful information in addition to carbonate and bicarbonate relationships.

2.1.3.2. Chloride

Thiocyanate ion is liberated from mercuric thiocyanate by the formation of non-ionic but soluble mercuric chloride. In the presence of ferric ion, the liberated thiocynate forms a highly colored ferric thiocyanate whose concentration is proportional to the original chloride concentration. The intensity of the ferric thiocyanate was measured spectrophotometrically.

2.1.3.3. Dissolved Metals

Dissolved metals in the acidified aliquots of filtered trench waters were determined by atomic absorption spectroscopy.

2.1.3.4. Ferrous--Ferric Iron

Iron in the ferrous state was reacted with 1,10-phenanthroline between pH 3.2 and 3.3. The orange-red ferrous-phenanthroline complex was measured spectrophotometrically. Ferric iron was determined by subtracting the ferrous iron concentration from the total iron concentration. Total iron was determined colorimetrically by reduction with hydroxylamine hydrochloride and subsequent reaction with 1,10-phenanthroline. Atomic absorption determination of total iron was a convenient check on this method.

2.1.3.5. Fluoride

Fluoride was determined with a specific ion electrode consisting of a single-crystal lanthanum fluoride membrane and an internal reference. The crystal is an ionic conductor in which only fluoride ions are mobile. The potential developed across the membrane in the Orion 94-09 probe is proportional to the fluoride ions in solution and was measured against an external reference with the Orion 407A specific ion meter.

2.1.3.6. Phosphate

The determination of orthophosphate involved the formation of molybdophosphoric acid with the addition of ammonium molybdate in acid medium. This was reduced to molybdenum blue by ascorbic acid at 37°C and measured spectrophotometrically.

2.1.3.7. Nitrogen-Ammonia

A gas sensing electrode, containing a hydrophobic gas permeable membrane, allows dissolved ammonia generated in the sample to diffuse through the membrane until the partial pressure of ammonia is the same on both sides. The partial pressure of ammonia is proportional to its concentration according to Henry's law. When sodium peroxide and sodium hypochlorite are added to a solution containing an ammonium salt, the Berthelot reaction takes place with the formation of a green compound related to endophenol. The color intensity was measured spectrophotometrically which is proportional to the ammonia concentration. Methods have been developed at BNL to perform this analysis in an inert nitrogen or argon environment.

2.1.3.8. Nitrogen-Nitrate

Nitrite reacts with sulphanilamide under acidic conditions to yield a diazo compound which couples with N-1-napthylethylene-diamine dihydrochloride to form a red colored compound. The color intensity measured spectrophotometrically was related to the concentration of nitrite.

2.1.3.9. Nitrogen-Nitrite plus Nitrate

Nitrate was reduced to nitrite when passed through a cadmium-copper column. The nitrite was then treated with sulphanilamide and N-1-naphthylenediamine dihydrochloride to form the red azo dye as above. When both nitrite and nitrate were present in a sample, the nitrate content was obtained by subtracting the nitrite value from the combined nitrite plus nitrate value.

2.1.3.10. Silica

Ammonium molybdate reacts with silicic acid (H_4SiO_4) in acid medium to form molybdosilicic acid. This was reduced to molybdenum blue by ascorbic acid and measured spectrophotometrically. Oxalic acid was added before the ascorbic acid to eliminate interference from phosphates.

2.1.3.11.. Sulphate

When equimolar barium chloride and methylthymol blue are added to a sulfate-containing sample at pH 2.5-3.0, barium sulphate precipitates. After adjusting the pH to 12.5-13.0, the barium remaining in solution reacts with the methylthymol blue to form a chelate. The uncombined methylthymol blue remaining in solution was measured spectrophotometrically and was proportional to the sulphate initially present in the sample.

2.1.3.12. Sulphide

A silver-silver sulphide electrode used in conjunction with a reference electrode develops a potential which is a direct function of the logarithm of the activity of the sulphide ion. The sulphide electrode was calibrated using the method developed by Berner (1963).

2.1.4. Organic Constituents

2.1.4.1. Dissolved Carbon

The total dissolved carbon and inorganic carbon contents were determined using a Beckman Model 915 Total Carbon Analyzer. The difference between the total dissolved carbon and the inorganic carbon measurements is the dissolved organic carbon (DOC) content of the sample.

2.1.4.2. Organic Carbon Compounds

A liquid extraction technique using methylene chloride was employed to isolate acidic, neutral, and basic hydrophobic organic compounds from the trench waters. These fractions were analyzed by gas chromatography and identified by mass spectrometry (GC/MS) methods.

Hydrophilic compounds were isolated at PNL using BF_3 in methanol to prepare methylated derivatives which were also analyzed by gas chromatography and identified by mass spectroscopic methods (GS/MS).

2.1.5. Radiochemical Constituents

Radiochemical measurements were performed on the filtrate and particulates collected following filtration of each trench water sample. Except for tritium, all of the radiochemical measurements were made on an acidified aliquot of the filtrate. Tritium was measured on a non-acidified fraction of filtrate. The following is a brief summary of the procedures used to measure radionuclides in trench and well waters.

2.1.5.1. Gross Alpha/Gross Beta

An aliquot of acidified filtrate was heated to dryness in a 50 mm planchette and counted with a Canberra model 2200 low-level alpha/beta gas flow proportional counter. Each sample was counted at two instrument settings corresponding to the plutonium-239 alpha plateau and the strontium-90/yttrium-90 beta plateau. This measurement was not made for the particulate fraction. Gross counting should be regarded as a rapid, semi-quantitative measure of sample activity.

2.1.5.2. Tritium

An aliquot of tritiated water, distilled by conventional methods at atmospheric pressure, was emulsified with Packard Insta-Gel liquid scintillation reagent and counted in a Searle Analytic-92 liquid scintillation counter.

2.1.5.3. Strontium-90

Strontium-90 was determined by radiochemically separating strontium from the trench water sample and counting the in-growth of yttrium-90 with a low-level beta counter. These determinations were made by LFE Laboratories, Richmond, California.

2.1.5.4. Plutonium-238,239,240

Plutonium isotopes were radiochemically separated from other alpha emitting radionuclides by anion exchange chromatography and electroplated onto a counting disc. Plutonium isotopes on the disc were measured by alpha spectroscopy with a surface barrier silicon detector. The Pu isotopes were analysed by LFE Laboratories, Richmond, California.

2.1.5.5. Gamma-Ray Emitters

Gamma-ray emitting radionuclides, such as Am-241, Cs-137, Cs-134, Co-60, Na-22, and Mn-54, were measured by counting aliquots of the filtered trench water with a 2 keV resolution Ge(Li) detector. Radionuclide identifications were made on the basis of measured gamma ray energies and relative peak heights of nuclides emitting more than one gamma.

3. RESULTS OF LEACHATE CHEMISTRY

3.1 Selection of Leachate Data

As reported earlier, several sampling trips were undertaken by BNL to Maxey Flats disposal site during the period 1976-1981 to collect trench and well water samples. In many instances, the same trench was sampled multiply during subsequent sampling trips.

During the April 1976 preliminary study sampling trip, adequate precautions were not taken to prevent air from coming in contact with water samples during collection. Consequently, the water samples do not represent the actual leachates in the trenches. We consider these data suspect and have not discussed them further in this report.

The samples collected during the 1977 survey study sampling trip were analyzed for radionuclides as well as dissolved organic carbon. The major constituents, however, were not determined. Consequently, we have considered the radionuclide data based on the survey study to evaluate the distributions of radionuclides present in the various trenches at the disposal site.

The leachate samplings conducted in September 1976, July 1977, May 1978, October 1979, and October 1981 involved use of anoxic sampling procedures. In addition, the leachate analyses were relatively complete in that most of the samples were analyzed for major ion constituents, radionuclides, and in many cases for organic constituents.

An ion balance of the major cations and anions present in each leachate sample was conducted to determine the completeness of the trench water analyses. Equivalents of cation and anions sums were compared to calculate the ion balance error. Table 3.1 gives the percent error in ion balance for each water sample collected during the five sampling trips. In most cases, we found the error in ion balance to be less than 10%, indicating that these analyses are relatively complete and accurate. However, eight leachate samples exhibited appreciable error in ion balance. As a result, these data have been excluded from further consideration. Based on a relatively small ion balance error, we have compiled in Table 3.2 a list of trench water samples that will be considered further in the interpretation of trench leachate compositions. It should be noted, however, that for the interpretation of radionuclide and organic data all leachate samples have been considered, since these constituents are present in trace amounts and do not contribute significantly to bulk composition of the trench leachates.

Table 3.1. Ion balance of major anions and cations for Maxey Flats trench leachates.

Trench	Sampling Date	Σ Cations (meq/L)	Σ Anions (meq/L)	Error[a] (%)
2	9/76	42	40	2.4
2	7/77	65	52	11
7	9/76	29	28	1.7
7	10/81	129	124	2.0
18	9/76	42	50	-8.7
19s	9/76	25	24	2.0
19s	5/78	46	22	35
19s	11/79	39	24	24
19s	10/81	29	28	1.8
23	10/81	65	68	-2.3
26	9/76	26	35	-15
26	7/77	34	23	19
27	9/76	143	129	5.1
27	5/78	104	117	-5.9
27	10/79	194	180	3.7
27	10/81	81	76	3.2
30	10/79	157	135	7.5
32	9/76	59	65	-4.8
32	7/77	128	67	31
32	10/79	351	44	78
33L4	9/76	81	47	27
33L4	5/78	42	38	5.0
33L4	10/81	56	53	2.8
33L8	10/81	21	23	-4.5
33L9	9/76	123	82	20
33L18	5/78	20	169	-79
35	10/81	59	55	3.5
37	9/76	144	175	-9.7

[a] The percent ion balance error was estimated using the relationship:

$$\text{Percent Error} = \frac{\Sigma c - \Sigma a}{\Sigma c + \Sigma a} \cdot 100$$

where Σc and Σa represent cation and anion sums (meq/L), respectively.

An on-site well UB1A was sampled several times by BNL during the study period to obtain baseline information on ambient groundwater characteristics. Analyses of the well water samples revealed the presence of contaminants such as radionuclides and dissolved organic compounds, presumably derived from neighboring trenches. Consequently, the composition of an off-site well UA3, which is the shallowest of UA series wells (Zehner, 1983), was selected for baseline information. The water in this well is derived from rock units corresponding to lower part of Nancy Member and upper part of Farmers Member. According to Zehner (pers. comm.), well water UA3 may be used as a substitute for UB1A to represent ambient groundwater composition.

Table 3.2. Selected trench leachates considered in this study.

Trench	Sampling Date	Leachate Designation
2	9/76	2(76)
7	9/76	7(76)
7[a]	10/81	7(81)
18	9/76	18(76)
19s	9/76	19s(76)
19s[a]	10/81	19s(81)
23[a]	10/81	23(81)
26	9/76	26(76)
27	9/76	27(76)
27	5/78	27(78)
27	10/79	27(79)
27	10/81	27(81)
30	10/79	30(79)
32	9/76	32(76)
33L4	5/78	33L4(78)
33L4	10/81	33L4(81)
33L8	10/81	33L8(81)
35	10/81	35(81)
37	9/76	37(76)

[a] Samples taken from these trenches during the 1981 sampling trip have been designated as 7-3, 19W and 23M in a previous report (Dayal et al., 1984). The number or letter suffix corresponds to a particular riser pipe that was used for sampling trench water at that particular time.

The major ion compositions of UA3 well waters sampled in 10/78, 6/79, and 10/79 by USGS personnel as reported by Zehner (1983) are given in Table 3.3. In our interpretation of leachate data, we have used the average composition of UA3 to represent ambient groundwater composition.

Table 3.3. Major ion composition of well water UA3.[a]

	Concentration (mg/L)			
Constituents	UA3 (10/78)	UA3 (6/79)	UA3 (10/79)	UA3 (Av)
Calcium	280	180	200	220
Magnesium	430	350	370	380
Potassium	37	18	17	24
Sodium	350	280	220	300
Ammonium	b	b	b	<1[d]
Iron (total)	b	b	b	<0.1[d]
Manganese (total)	b	b	b	<0.1[d]
Alkalinity (as $CaCO_3$)	484	434	459	459
Chloride	77	67	67	70
Sulphate	2400	2000	1900	2100
Nitrate + Nitrate (as N)	b	c	0.2	0.2
Silica	8	10	9	9
pH	b	7.0	6.8	6.9
Total Dissolved Solids	4430	3980	3700	4040
Dissolved Organic Carbon	b	b	b	6.2[d]
Dissolved Inorganic Carbon	b	b	b	1.5[d]

[a] UA3 is the shallowest of the off-site UA series wells. The water is derived from rock units corresponding to lower part of Nancy Member and upper part of Farmers Member (Zehner, 1983). The water samplings and analyses were conducted by USGS personnel.

[b] Not determined.

[c] Below detection.

[d] Not determined in UA3 well water; the values given are those based on well water UB1A composition.

3.2 Field Parameters

Field data on specific conductance, dissolved oxygen, Eh, pH, sulphide, and temperature for the selected trench leachates are given in Table 3.4.

The sulphide data ($E_S 2-$, mV), based on silver/silver sulphide calomel electrode pair measurements in the field, were converted to sulphide concentrations using the calibration curve obtained in the laboratory (Figure 3.1). Figure 3.1 shows good agreement between BNL data and data reported earlier by Berner (1963). The curve in Figure 3.1 is represented by the equation

$$E_S 2- = -0.891 + 0.0294 \, pS^{2-} \qquad (3.1)$$

where $E_S 2-$ represents the measured sulphide potentials and pS^{2-} the sulphide activity. Equation (3.1) was used to convert measured sulphide potentials into sulphide concentrations as follows:

Using the sulphide equilibria equations,

$$K_{H_2S}\,K_{HS^-} = \frac{[S^{2-}]\,[H^+]^2}{[H_2S]} \qquad (3.2)$$

$$[H_2S] = \frac{[S^{2-}][H^+]^2}{K_{H_2S}\,K_{HS^-}} = \frac{[S^{2-}]\,[H^+]^2}{10^{-20.9}} \qquad (3.3)$$

the $K_{H_2S}K_{HS^-}$ value of $10^{-20.9}$ (Morel, 1983), and the measured pH and calculated sulphide activities, we estimated the H_2S concentrations in the trench leachates as given in Table 3.4.

Table 3.4. Field parameters of trench leachates.

Trench	Temperature (°C)	pH	Eh (mV)[a]	Dissolved Oxygen (ppm)	Specific Conductance (μMho/cm)	Sulphide ($E_S{}^{2-}$, mV)[b]	H_2S (mg/L)[c]
2(76)	20.0	6.7	d	d	3400	d	
7(76)	22.5	6.9	d	d	2530	d	
7(81)	16.5	7.4	-44	0.10	12000	-324	2.2×10^{-15}
18(76)	21.5	7.0	d	d	3450	d	
19s(76)	21.0	6.6	d	d	2340	d	
19s(81)	15.0	6.5	-28	0.10	2100	-465	8.5×10^{-9}
23(81)	17.0	7.5	-39	0.05	4800	-302	2.7×10^{-16}
26(76)	21.0	6.8	d	d	2910	d	
27(76)	20.0	6.0	d	d	120000	d	
27(78)	17.6	6.6	+17	0.05	9370	d	
27(79)	18.0	5.9	+140	0.15	18000	-490	1.1×10^{-6}
27(Av)[e]	18.5	6.2	+79	0.10	13120	-490	2.7×10^{-7}
27(81)	16.0	6.8	+17	<0.05	6000	-353	3.4×10^{-13}
30(79)	16.0	6.5	+140	0.10	6900	-0.9	1.4×10^{-24}
32(76)	20.0	7.3	d	d	5750	d	
33L4(78)	12.0	12.1	-7	4.1	5580	d	
33L4(81)	17.0	12.0	-54	0.05	6400	-278	4.3×10^{-26}
33L8(81)	18.0	6.0	-135	0.25	2000	-125	2.7×10^{-19}
35(81)	17.0	8.2	-14	0.10	3400	-486	1.7×10^{-11}
37(76)	20.0	5.1	d	d	6900	d	

[a] Field measurements of Eh are reported relative to the Standard Hydrogen Electrode (SHE).

[b] The sulphide electrode was calibrated in the laboratory using the method developed by Berner (1963).

[c] Calculated based on measured sulphide potentials, pH, and the known equilibrium constants for the sulphide system.

[d] Not measured.

[e] Average values for trench leachate 27 based on values reported for 9/76, 5/78 and 10/79 samplings.

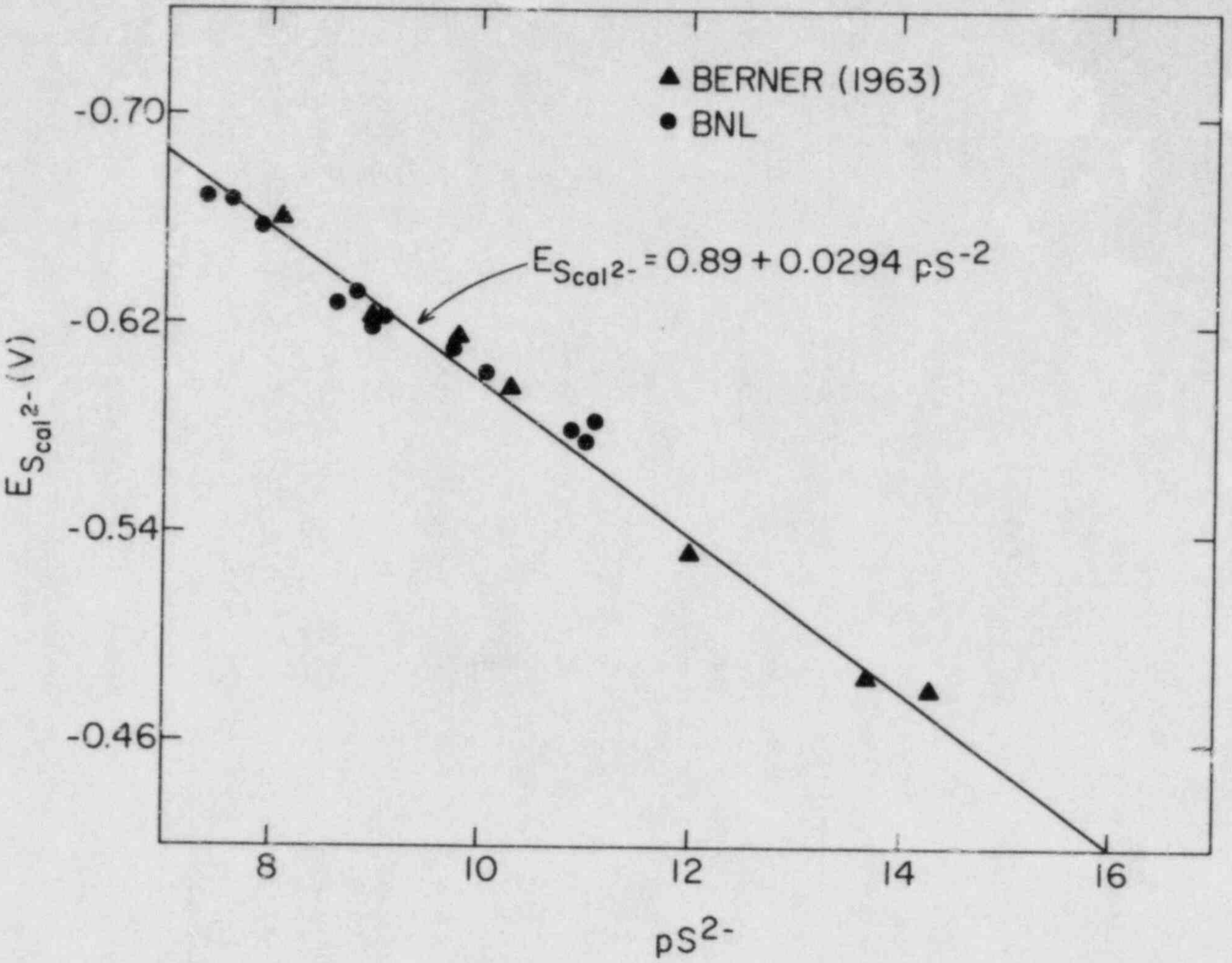


Figure 3.1. Calibration curve of the silver-silver sulphide electrode. E_{Scal}^{2-} corresponds to the measured potential relative to the calomel electrode. Data reported by Berner (1963) are also presented (●).

The results show that most leachates are depleted in dissolved oxygen indicating anoxic conditions in the trenches. Anoxic conditions are also indicated by negative redox potentials and the presence of sulphide in most leachates.

The pH data show that most trench leachates exhibit pH in the range of 6.0 to 8.5 pH units. Highly alkaline conditions are observed in trench 33L4 (pH ≈ 12).

Relative to most trench leachates, leachates 7 and 27, both sampled prior to 1981, exhibit the highest specific conductance.

The calculated H_2S concentrations range from a low of 10^{-24} mg/L in leachate 33L4(81) to a high of 10^{-6} mg/L in leachate 27(79).

3.3 Cation Composition

The concentrations of the various cations present in the trench leachates are shown in Table 3.5.

The levels of ammonium concentrations observed range from 18 mg/L in leachate 33L4(78) to 116 mg/L in leachate 27(81). Relative to the ambient groundwater ammonium concentration of <0.1 ppm, all leachates sampled exhibit considerable enrichment in ammonium.

The calcium and magnesium concentrations of most trench leachates and well water UA3 lie in the 0-400 mg/L range. The highest concentrations of Mg^{2+} (1300 mg/L) and Ca^{2+} (864 mg/L) are observed in leachates 30(79) and 33L4(81), respectively.

The sodium and potassium concentrations observed for most trench leachates lie in the 20-1000 mg/L and 10-140 mg/L ranges, respectively. The highest concentrations of both Na^+ (2140 mg/L) and K^+ (329 mg/L) are observed in leachate 7(81). Relative to well water UA3, both Na^+ and K^+ are significantly enriched in most trench leachates.

Most trench leachates exhibit dissolved iron and manganese concentrations in the range of 0-65 mg/L and 0-2 mg/L, respectively. The highest concentrations are observed in leachates 37(76) and 27(79) in the range of 1100-1400 mg/L for iron and 42-190 mg/L for manganese. Leachates such as 33L4(78,81) and 35(81) which show the lowest concentrations of dissolved iron are also depleted in dissolved manganese. As shown in Table 3.5, in most cases, the dissolved iron present in the leachates occurs in the ferrous state. Relative to ambient groundwater concentrations, both dissolved Fe and Mn are significantly enriched in most leachates.

Table 3.5. Cation composition of trench leachates.

Trench	Concentration (mg/L)										
	Na^+	K^+	NH_4^+	Li^+	Fe_T[a]	Fe^{2+}	Mn_T[a]	Ca^{2+}	Mg^{2+}	Ba^{2+}	Sr^{2+}
2(76)	700	66	b	0.99	40	b	0.8	29	79	b	b
7(76)	240	140	b	0.56	61	b	0.5	130	73	b	b
7(81)	2140	329	75	b	17	12	1.9	107	193	<0.5	0.7
18(76)	540	50	b	18	33	b	<0.1	14	160	b	b
19s(76)	100	25	b	9.2	150	b	0.8	58	130	b	b
19s(81)	231	27	45	b	65	62	0.5	49	128	0.7	0.6
23(81)	825	77	100	b	7	6	<0.1	11	230	<0.5	<0.3
26(76)	20	39	b	0.34	65	b	0.7	31	130	b	b
27(76)	670	120	b	1.9	1200	b	70	600	430	b	b
27(78)	450	36	80	1.9	1150	b	88	240	255	b	4
27(79)	770	100	60	2.3	1400	1360	190	740	720	17	7
27(Av)[c]	495	85	70	2.0	1250	1360	116	455	468	17	5
27(81)	554	87	116	b	165	164	1.7	220	350	15	2.3
30(79)	1000	43	50	<0.5	10	10	0.3	32	1300	<2.0	<0.3
32(76)	700	210	b	0.15	16	b	1.2	75	230	b	b
33L4(78)	180	30	18	0.16	0.3	b	<0.1	650	0.1	7.0	b
33L4(81)	180	102	26	b	0.2	b	<0.1	864	<0.2	7.3	8
33L8(81)	50	11	50	b	43	42	1.8	190	49	<0.5	<0.3
35(81)	614	51	37	b	0.9	0.8	0.3	26	330	<0.5	<0.3
37(76)	680	20	b	0.30	1100	b	42	250	730	b	b

[a] Represent total dissolved iron (Fe_T) and total dissolved manganese (Mn_T).

[b] Not measured.

[c] Average composition based on data reported for 9/76, 5/78, and 10/79 samplings.

Other cation constituents, such as Li^+, Ba^{2+}, and Sr^{2+}, have also been detected. In most leachates, lithium concentrations are below 1 mg/L. However, leachates 18(76) and 19s(76) show significant enrichment at levels of 18 mg/L and 9 mg/L, respectively. In most trench leachates, Ba^{2+} and Sr^{2+} concentrations are low to below detection with the exception of leachates 27(79,81) and 33L4(78,81) where substantial enrichment is observed. Both Ba^{2+} and Sr^{2+} appear to be enriched in leachates which also show enrichment in Ca^{2+}.

3.4 Anion Composition

The concentrations of the major anions present in the trench leachates are given in Table 3.6.

Table 3.6. Anion composition of trench leachates.

Trench	Concentration mg/L					
	Cl$^-$	F$^-$	NO$_3^-$ + NO$_2^-$ (as N)	Alkalinity (as CaCO$_3$)	SO$_4^{2-}$	SiO$_2$
2(76)	310	a	<0.05	1560	11	14
7(76)	220	a	<0.05	1090	<10	12
7(81)	2500	44	9	1150	1320	a
18(76)	310	a	<0.05	2050	18	13
19s(76)	150	a	<0.05	980	<10	9
19s(81)	231	4.0	0.53	1040	<1.5	a
23(81)	575	5.3	28	2420	57	a
26(76)	290	a	<0.05	1320	<10	9
27(76)	4200	a	1.6	432	69	14
27(78)	3900	0.9	0.10	330	<0.5	5
27(79)	6100	a	0.75	300	2.2	19
27(Av)[b]	4733	0.9	0.82	354	24	13
27(81)	2340	a	17	312	<1.5	a
30(79)	4	a	0.11	6400	85	42
32(76)	370	a	<0.05	2720	11	14
33L4(78)	168	a	11	1600	<5	1
33L4(81)	361	a	10	2120	<1.5	a
33L8(81)	37	3.7	1.6	1080	15	a
35(81)	235	45	0.67	2310	<1.5	a
37(76)	180	a	13	125	8000	35

[a] Not measured.

[b] Average composition based on data reported for 9/76, 5/78 and 10/79 samplings.

Most trench leachates exhibit chloride concentrations in the 30-600 mg/L range. Leachates 7(81) and 27(76,78,79) exhibit much higher concentrations in the range of 2300-6100 mg/L. The lowest chloride concentration (4 mg/L) is observed in leachate 30(79). Relative to well water UA3, most leachates show significant enrichment in Cl$^-$. Relatively high concentrations of fluoride ($\approx$45 mg/L) are observed in leachates 7(81) and 35(81).

The nitrate concentrations in the various leachates vary from <0.05 mg/L in several trenches to 28 mg/L in leachate 23(81). Relative to ambient groundwater concentration, nitrate shows enrichment in several trench leachates.

The results of silica analyses conducted on leachates sampled prior to 1981 show that for most leachates the silica concentrations lie in the range of 1-15 mg/L SiO$_2$. Relatively high concentrations of 35 mg/L and 42 mg/L are observed in leachates 37(76) and 30(79), respectively. In the pH range of 6 to 9 pH units, the dominant form of dissolved silica is monomeric silicic acid, whereas under extreme acidic and alkaline conditions, the ionic, polymeric forms of silicic acid dominate (Duedall, Dayal, and Willey, 1976).

The sulphate concentrations for most trench leachates range from below detection to 90 mg/L. Elevated concentrations of 1320 mg/L and 8000 mg/L are observed in leachates 7(81) and 37(76). It is interesting to note that elevated concentrations of silica are also observed in the same leachates. Relative to the sulphate concentration of 2100 mg/L in well water UA3, it should be noted that most trench leachates show significant sulphate depletion.

The titration alkalinities measured for the various trench leachates show that most leachates represent well-buffered systems and exhibit a wide distribution, ranging from 100 to ≈2700 mg/L. The highest alkalinity is observed in leachate 30(79). Relative to the ambient groundwater alkalinity, all leachates exhibit significant enrichment.

3.5 Major Water Types

In Figure 3.3, the cation and anion equivalents are displayed on Piper trilinear diagrams to graphically represent the dissolved constituents in trench leachates and to help classify distinct water types. For the sake of comparison, the average composition of well water UA3 is also projected on the diamond shaped field to show its distinct chemical identity. In terms of their anion contents, the trench leachates can be classified into two distinct water types:

(a) Bicarbonate rich ($HCO_3^- + CO_3^{2-} > SO_4^{2-} + Cl^-$):
2(7[illegible]), 7(76), 18(76), 19s(76,81), 23(81), 26(76), 30(79), 32(76), 33L4(78,81), 33L8(81), and 35(81).

(b) Bicarbonate poor ($HCO_3^- + CO_3^{2-} < SO_4^{2-} + Cl^-$):
7(81), 27(Av), 27(81), 37(76), and UA3.

In terms of both anion and cations contents, the leachates can be classified, as shown in Table 3.7, into several groupings of specific water types.

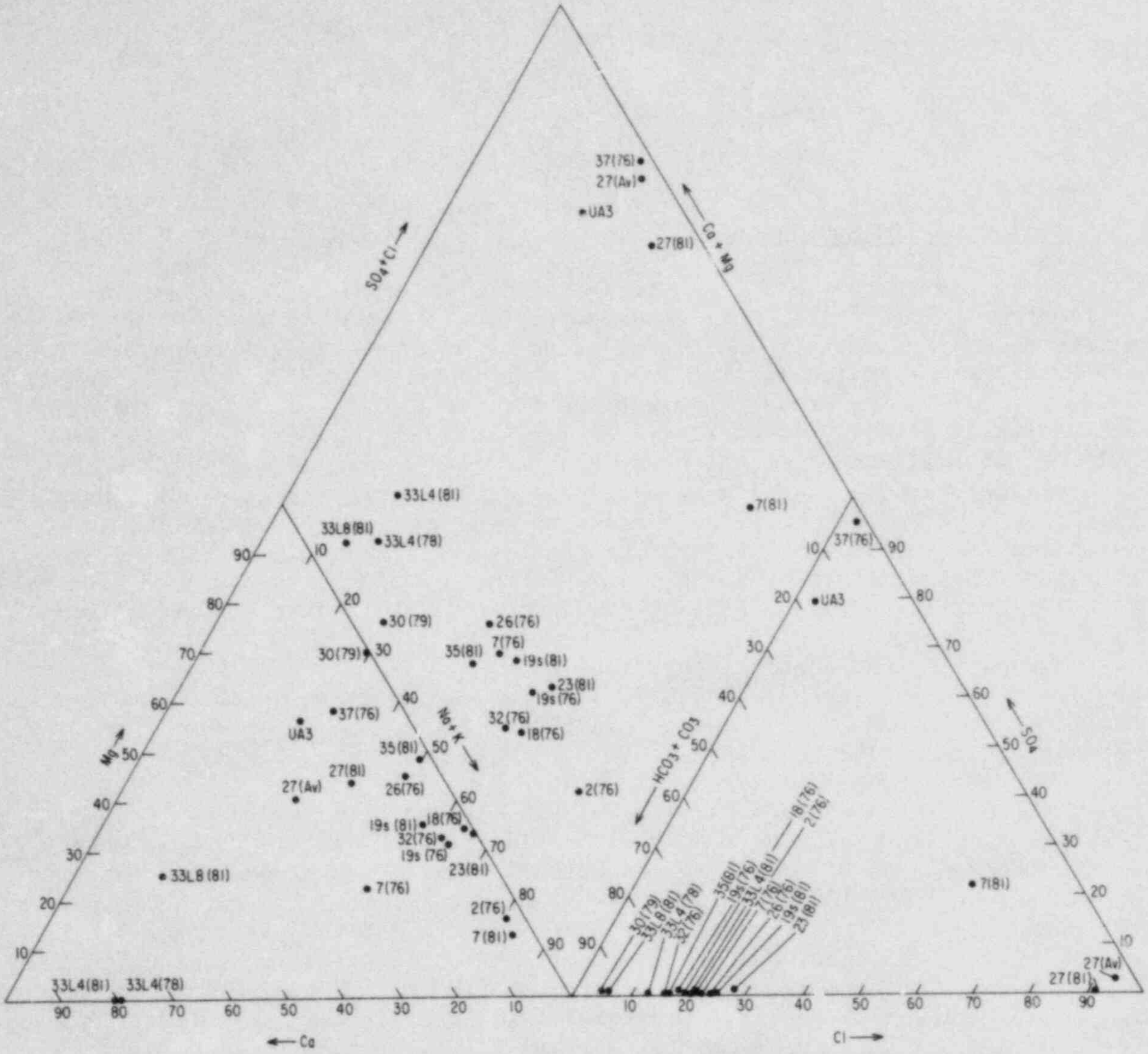


Figure 3.3. Piper trilinear diagram showing the different water types representing trench leachates and ambient groundwater.

Table 3.7. Various water types showing chemical variability in trench leachates.

Leachate	Water Type
2(76), 7(76), 18(76), 19s(76,81), 23(81), 26(76), 30(79), 32(76), 35(81)	(Na + K) - Mg - HCO_3
37(76), UA3	Mg - (Na + K) - SO_4
7(81)	(Na + K) - Cl
27(Av), 27(81)	(Na + K) - Mg - Cl
33L4(78,81), 33L8(81)	Ca - HCO_3

3.6 Dissolved Radionuclides

There are two sets of data presented on dissolved radionuclides observed in the trench leachates. During the survey study conducted in 1977, leachates were sampled from most of the burial trenches at Maxey Flats (trench 1 through trench 44) and analyzed for tritium and gamma emitting radionuclides. The results of 1977 survey study represent the first set of complete data for dissolved radionuclides present in trench leachates and, to our knowledge, is the only set of available data that provides information on the distributions of several important radionuclides in all the trench leachates sampled at Maxey Flats. The second set of data is based on decay corrected average values of dissolved radionuclides in trench leachates sampled multiply during the six sampling trips undertaken by BNL from 1976 through 1981. This set of data also includes the radionuclide data based on the 1977 survey study.

The survey study data given in Table 3.8 and displayed in Figure 3.4 show that Co-60, Cs-137, Am-241, and Cs-134 are the major gamma emitting radionuclides identified in the trench leachates. In addition, Mn-54 and Na-22 were detected in several trenches.

Tritium, which was also analyzed in the leachates, is found to be the most abundant among all the radionuclides identified. All leachates exhibit substantial amounts of H-3, with leachate 30 showing the highest concentration at a level of 7.4×10^9 pCi/L and leachate 14L the lowest concentration (2.5×10^5 pCi/L). It is important to note that leachate samples taken from the same trench but at different sumps show significant differences in their H-3 concentrations. For example, leachates 31E and 31W and 36E and 36W represent leachate samples collected from east and west sumps of trenches 31 and 36, respectively. Similarly, leachates 44N and 44S correspond to leachates sampled at the north and south sumps of trench 44.

The survey study results show that Am-241 was below detection in most trench leachates. However, several trenches did contain appreciable amounts of Am-241. The highest Am-241 concentration, at a level of 9.3×10^3 pCi/L, is observed in leachate 37.

Cs-134 is found to be below the limits of detection in most trench leachates. Only nine leachate samples contain measurable quantities of Cs-134, with leachate 40N showing the highest concentration (2.2×10^4 pCi/L). Measurable quantities of Cs-137 are found in at least 23 trenches. Like Cs-134, the highest concentration of Cs-137 is also observed in leachate 40N (1.5×10^5 pCi/L). It is important to note that practically all leachates sampled from the "L" series trenches, where a large fraction of the waste dumped was in liquid form and subsequently solidified, contain both cesium isotopes in quantities below their detection limits. Only trenches 33L3 and 33L18 contain substantial amounts of Cs-137 and Cs-134 in solution.

Table 3.8. Tritium and gamma emitting radionuclides in trench leachates based on 1977 survey study [activity, pCi/L ($\pm 2\sigma\%$)][a]

Trench	H-3	Am-241	Cs-134	Cs-137	Co-60
1	$3.7\text{x}10^{6}$ (3.5)	$<1.7\text{x}10^{2}$	$<1.3\text{x}10^{2}$	$<1.9\text{x}10^{2}$	$<2.7\text{x}10^{2}$
2	$1.9\text{x}10^{7}$ (1.6)	$4.7\text{x}10^{3}$ (6.2)	$<1.7\text{x}10^{2}$	$<2.3\text{x}10^{2}$	$1.9\text{x}10^{4}$ (3.1)
3	$1.3\text{x}10^{7}$ (1.9)	$<1.9\text{x}10^{2}$	$<1.4\text{x}10^{2}$	$<2.0\text{x}10^{2}$	$1.9\text{x}10^{3}$ (12)
5S	$1.5\text{x}10^{8}$ (<1)	$<1.7\text{x}10^{2}$	$<2.2\text{x}10^{2}$	$<2.9\text{x}10^{2}$	$9.0\text{x}10^{2}$ (24)
7	$3.6\text{x}10^{8}$ (<1)	$<6.7\text{x}10^{2}$	$<2.5\text{x}10^{2}$	$3.3\text{x}10^{3}$ (12)	$8.5\text{x}10^{4}$ (1.4)
8	$6.4\text{x}10^{5}$ (8.4)	$<2.7\text{x}10^{2}$	$<2.6\text{x}10^{2}$	$9.0\text{x}10^{2}$ (29)	$1.2\text{x}10^{5}$ (1.2)
9L	$7.9\text{x}10^{5}$ (7.6)	$<4.0\text{x}10^{1}$	$<1.6\text{x}10^{1}$	$<2.0\text{x}10^{1}$	$<2.0\text{x}10^{1}$
14L	$2.5\text{x}10^{5}$ (13)	$<1.7\text{x}10^{2}$	$<1.4\text{x}10^{2}$	$<1.7\text{x}10^{2}$	$<1.6\text{x}10^{2}$
17L	$8.9\text{x}10^{6}$ (2.3)	$<1.9\text{x}10^{2}$	$<1.2\text{x}10^{2}$	$<1.5\text{x}10^{2}$	$<1.5\text{x}10^{2}$
18	$4.5\text{x}10^{8}$ (<1)	$<2.2\text{x}10^{2}$	$<1.6\text{x}10^{2}$	$4.8\text{x}10^{3}$ (6.8)	$2.3\text{x}10^{4}$ (2.8)
19S	$8.4\text{x}10^{7}$ (<1)	$<2.8\text{x}10^{2}$	$<1.2\text{x}10^{2}$	$4.6\text{x}10^{3}$ (5.2)	$1.3\text{x}10^{3}$ (13)
22	$1.8\text{x}10^{6}$ (5.1)	$<1.8\text{x}10^{2}$	$<1.2\text{x}10^{2}$	$<1.7\text{x}10^{2}$	$1.5\text{x}10^{3}$ (13)
23	$1.0\text{x}10^{9}$ (<1)	$<1.8\text{x}10^{2}$	$<1.1\text{x}10^{2}$	$<1.6\text{x}10^{2}$	$<1.6\text{x}10^{2}$
24	$1.9\text{x}10^{8}$ (<1)	$9.0\text{x}10^{2}$ (34)	$<1.4\text{x}10^{2}$	$4.3\text{x}10^{2}$ (19)	$1.2\text{x}10^{3}$ (15)
25	$8.0\text{x}10^{8}$ (<1)	$<1.7\text{x}10^{2}$	$<1.3\text{x}10^{2}$	$3.3\text{x}10^{2}$ (15)	$<1.2\text{x}10^{2}$
26[b]	$1.1\text{x}10^{8}$ (<1)	$1.0\text{x}10^{3}$ (9.5)	$7.0\text{x}10^{1}$ (29)	$4.4\text{x}10^{3}$ (2.0)	$4.6\text{x}10^{2}$ (8.6)
27[c]	$4.8\text{x}10^{9}$ (<1)	$2.7\text{x}10^{3}$ (10)	$5.7\text{x}10^{2}$ (16)	$5.6\text{x}10^{3}$ (2.1)	$1.3\text{x}10^{4}$ (1.4)
30	$7.4\text{x}10^{9}$ (<1)	$<2.8\text{x}10^{2}$	$<2.9\text{x}10^{2}$	$9.2\text{x}10^{4}$ (1.1)	$3.0\text{x}10^{4}$ (2.4)
31E	$4.8\text{x}10^{8}$ (<1)	$3.0\text{x}10^{2}$ (62)	$<1.4\text{x}10^{2}$	$7.6\text{x}10^{2}$ (4.0)	$3.6\text{x}10^{3}$ (7.7)
31W	$4.7\text{x}10^{9}$ (<1)	$7.0\text{x}10^{2}$ (23)	$9.9\text{x}10^{2}$ (6.1)	$4.0\text{x}10^{4}$ (<1)	$1.9\text{x}10^{3}$ (13)
32	$1.9\text{x}10^{9}$ (<1)	$<3.0\text{x}10^{2}$	$<1.6\text{x}10^{2}$	$4.2\text{x}10^{3}$ (5.7)	$2.2\text{x}10^{3}$ (13)
33L1	$3.7\text{x}10^{6}$ (3.5)	$<1.7\text{x}10^{2}$	$<1.2\text{x}10^{2}$	$<1.3\text{x}10^{2}$	$1.5\text{x}10^{3}$ (4.2)
33L3	$4.6\text{x}10^{7}$ (1.0)	$1.8\text{x}10^{3}$ (17)	$3.3\text{x}10^{3}$ (18)	$4.6\text{x}10^{4}$ (1.7)	$9.7\text{x}10^{4}$ (1.4)
33L4[d]	$5.9\text{x}10^{7}$ (1.3)	$2.0\text{x}10^{2}$ (47)	$<1.0\text{x}10^{2}$	$<2.0\text{x}10^{1}$	$<1.8\text{x}10^{2}$
33L6	$7.4\text{x}10^{6}$ (2.5)	$<1.5\text{x}10^{2}$	$<1.0\text{x}10^{2}$	$<1.2\text{x}10^{2}$	$3.7\text{x}10^{2}$ (9.5)
33L8	$1.3\text{x}10^{6}$ (5.1)	$<1.9\text{x}10^{2}$	$<1.7\text{x}10^{2}$	$<2.2\text{x}10^{2}$	$5.5\text{x}10^{3}$ (2.2)
33L9	$2.6\text{x}10^{7}$ (1.3)	$<1.7\text{x}10^{2}$	$<1.4\text{x}10^{2}$	$2.8\text{x}10^{3}$ (7.6)	$1.9\text{x}10^{3}$ (13)
33L10	$7.4\text{x}10^{5}$ (7.8)	$<1.5\text{x}10^{2}$	$<1.2\text{x}10^{2}$	$<1.7\text{x}10^{2}$	$1.1\text{x}10^{3}$ (14)
33L11	$2.2\text{x}10^{7}$ (1.4)	$<1.5\text{x}10^{2}$	$<1.2\text{x}10^{2}$	$<1.8\text{x}10^{2}$	$1.0\text{x}10^{3}$ (19)
33L12	$2.4\text{x}10^{7}$ (1.3)	$<1.9\text{x}10^{2}$	$<1.8\text{x}10^{2}$	$<2.5\text{x}10^{2}$	$3.4\text{x}10^{4}$ (2.4)
33L13	$5.7\text{x}10^{5}$ (8.9)	$<4.1\text{x}10^{1}$	$<1.8\text{x}10^{1}$	$<2.1\text{x}10^{1}$	$1.3\text{x}10^{3}$ (4.5)
33116	$1.3\text{x}10^{8}$ (<1)	$<5.4\text{x}10^{1}$	$<1.6\text{x}10^{1}$	$<1.8\text{x}10^{1}$	$<2.5\text{x}10^{1}$
33L17	$1.4\text{x}10^{7}$ (2.6)	$<1.5\text{x}10^{2}$	$<1.1\text{x}10^{2}$	$<1.8\text{x}10^{2}$	$1.3\text{x}10^{3}$ (16)
33L18	$5.0\text{x}10^{7}$ (<1)	$4.7\text{x}10^{3}$ (10)	$2.6\text{x}10^{3}$ (12)	$3.6\text{x}10^{4}$ (1.8)	$8.3\text{x}10^{3}$ (5.0)
34-1	$1.9\text{x}10^{6}$ (4.9)	$<3.4\text{x}10^{2}$	$1.6\text{x}10^{3}$ (21)	$2.8\text{x}10^{4}$ (2.0)	$1.0\text{x}10^{4}$ (4.3)
34-4	$9.9\text{x}10^{6}$ (2.2)	$<3.6\text{x}10^{2}$	$<3.9\text{x}10^{2}$	$<5.2\text{x}10^{2}$	$2.7\text{x}10^{5}$ (<1)
35	$2.4\text{x}10^{9}$ (<1)	$2.4\text{x}10^{2}$ (33)	$<1.7\text{x}10^{2}$	$5.1\text{x}10^{2}$ (12)	$<2.9\text{x}10^{2}$
36E	$5.3\text{x}10^{8}$ (<1)	$<1.7\text{x}10^{2}$	$<1.3\text{x}10^{2}$	$<2.0\text{x}10^{2}$	$1.4\text{x}10^{3}$ (16)
36W[e]	$5.1\text{x}10^{7}$ (<1)	$<1.8\text{x}10^{2}$	$3.0\text{x}10^{2}$ (90)	$6.7\text{x}10^{3}$ (4.2)	$2.4\text{x}10^{3}$ (11)
37[f]	$9.8\text{x}10^{6}$ (2.2)	$9.3\text{x}10^{3}$ (4.0)	$8.0\text{x}10^{2}$ (46)	$4.1\text{x}10^{3}$ (6.9)	$3.5\text{x}10^{4}$ (2.2)
38[g]	$3.3\text{x}10^{7}$ (1.2)	$5.0\text{x}10^{2}$ (57)	$<1.3\text{x}10^{2}$	$1.8\text{x}10^{3}$ (10)	$1.8\text{x}10^{3}$ (12)
39	$7.5\text{x}10^{5}$ (7.8)	$<4.1\text{x}10^{1}$	$<1.5\text{x}10^{1}$	$2.6\text{x}10^{2}$ (18)	$<1.9\text{x}10^{1}$
40N	$6.6\text{x}10^{8}$ (<1)	$<3.2\text{x}10^{2}$	$2.2\text{x}10^{4}$ (2.8)	$1.7\text{x}10^{5}$ (<1)	$2.8\text{x}10^{3}$ (11)
42[h]	$1.6\text{x}10^{7}$ (1.7)	$<1.6\text{x}10^{2}$	$<1.2\text{x}10^{2}$	$<1.8\text{x}10^{2}$	$2.8\text{x}10^{3}$ (9.2)
44N[i]	$1.0\text{x}10^{8}$ (<1)	$<6.4\text{x}10^{2}$	$7.0\text{x}10^{3}$ (32)	$1.5\text{x}10^{4}$ (7.2)	$8.4\text{x}10^{5}$ (<1)
44S[j]	$1.4\text{x}10^{7}$ (1.8)	$<4.1\text{x}10^{1}$	$<1.8\text{x}10^{1}$	$<2.7\text{x}10^{1}$	$4.7\text{x}10^{2}$ (7.8)

[a] Number in () = 2σ % counting uncertainty.
[b] Na-22 in trench 26 = $1.3\text{x}10^{2}$ (21).
[c] Mn-54 in trench 27 = $3\text{x}10^{2}$ (34).
[d] Na-22 in trench 33L4 = $1.3\text{x}10^{2}$ (20).
[e] Mn-54 in trench 36W = $2.1\text{x}10^{3}$ (14).
[f] Mn-54 in trench 37 = $1.8\text{x}10^{3}$ (26).
[g] Mn-54 in trench 38 = $9\text{x}10^{2}$ (28).
[h] Mn-54 in trench 42 = $6\text{x}10^{2}$ (33).
[i] Mn-54 in trench 44N = $1.9\text{x}10^{5}$ (1.3).
[j] Mn-54 in trench 44S = $1.7\text{x}10^{2}$ (24).

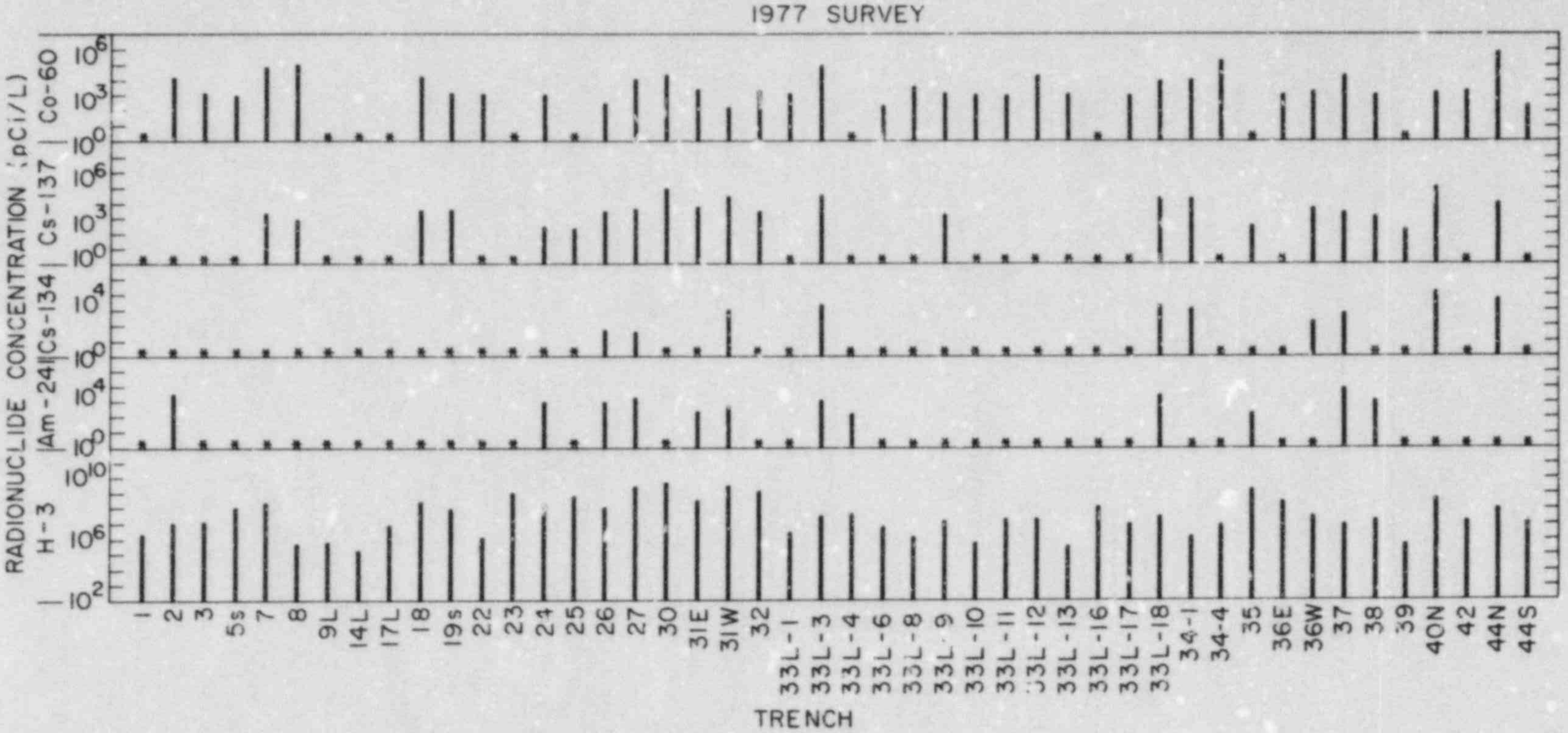


Figure 3.4. Radionuclide concentrations in trench leachates based on 1977 survey study. Asterisk (*) indicates radionuclide concentrations below the limits of detection.

Co-60 is observed in most trench leachates. Only ten trenches (1, 9L, 14L, 17L, 23, 25, 33L4, 33L16, 35, and 39) show immeasurably low concentrations of Co-60. The highest concentration is observed in leachate 44N (8.4 x 10^5 pCi/L), while leachate 44S contains Co-60 at a concentration level of 4.7 x 10^2 pCi/L.

In summary, tritium is the most abundant radionuclide observed in all leachates sampled. In contrast, Am-241 and Cs-134 are below their detection limits in many leachate samples. Leachate 40N exhibited the highest concentrations of both cesium isotopes. Co-60 is found to be present in most trench leachates, while the highest concentration is observed in leachate 44N. Invariably leachates sampled from the same trench but different sumps show significant differences in radionuclide concentrations. Except 33L3 and 33L18, all "L" series leachates contain immeasurably low concentrations of Am-241, Cs-134, and Cs-137. Co-60 is also below detection in several "L" series trenches (9L, 14L, 17L, 33L4, and 33L16).

The second set of data represents concentrations of radionuclides (decay corrected to October 1981) present in trench leachates sampled by BNL during the period 1976-1981 (Table 3.9). The decay corrected (October 1981), average radionuclide concentrations based on all BNL samplings during the period 1976-1981, are given in Table 3.10. This set of data also includes results of Sr-90, Pu-238, and Pu-239,240. In contrast to the large number of trenches sampled during the survey study, a relatively small number of selected trenches were sampled multiply during subsequent sampling trips.

The average radionuclide concentrations given in Table 3.10 are displayed in Figure 3.5. The error bars in Figure 3.5 reflect the extent of variation observed due to multiple leachate samplings in a given trench.

Among the radionuclides identified in the trench leachates, tritium is the most abundant ranging from 7 x 10^6 pCi/L in 33L8 to 1 x 10^{10} pCi/L in leachate 30. Following tritium, Sr-90 appears to be next most abundant ranging from ≈2 x 10^3 pCi/L in leachate 37 to 1 x 10^6 pCi/L in leachate 7. Most leachates exhibit Sr-90 concentrations in the range of 10^4 to 10^6 pCi/L.

Following tritium and Sr-90, both Co-60 and Cs-137 appear to be the next dominant radionuclides with most leachates showing a wide distribution in the observed concentrations ranging from 10^3 to 10^5 pCi/L. Both Co-60 and Cs-137 are relatively depleted in the "L" series trench leachates (33L4 and 33L8). Like Sr-90, the highest concentration of Cs-137 is observed in leachate 7. Co-60 also shows enrichment in leachate 7.

The Pu isotopes (Pu-238; Pu-239,240) exhibit a wide variation in the observed concentrations ranging from ≈10^0 to ≈10^5 pCi/L. Leachates 7 and 33L8 exhibit the lowest concentrations for both Pu isotopes, while the highest concentrations are observed in leachate 19s.

Table 3.9. Radionuclide concentrations in trench leachates sampled during the period 1976-1981.[a]

Radionuclide	Sampling Date	Trench 2	Trench 7	Trench 18	Trench 19s	Trench 23M	Trench 26	Trench 27	Trench 30
H-3	9/76	1.9x10^{7} (<1)	3.3x10^{8} (<1)	3.4x10^{8} (<1)	5.2x10^{7} (<1)	b	1.5x10^{8} (<1)	2.3x10^{8} (<1)	b
	6/77	1.5x10^{7} (1.6)	2.8x10^{8} (<1)	3.5x10^{8} (<1)	6.6x10^{7} (<1)	8.0x10^{8} (<1)	9.0x10^{7}	3.8x10^{9} (<1)	5.8x10^{9} (<1)
	7/77	1.6x10^{7} (<1)	b	b	b	b	1.0x10^{8} (<1)	b	b
	5/78	b	b	b	5.6x10^{7} (<1)	b	b	4.7x10^{8} (<1)	b
	10/79	b	b	b	7.8x10^{7} (<1)	b	b	4.6x10^{9} (<1)	1.6x10^{10} (<1)
	10/81	b	3.0x10^{8} (3)	b	9.8x10^{7} (6)	1.3x10^{9} (3)	b	1.9x10^{9} (3)	b
Sr-90	9/76	[illegible].0x10^{3} (<1)	1.8x10^{6} (<1)	4.2x10^{4} (<1)	2.3x10^{5} (<1)	b	3.1x10^{4} (<1)	1.8x10^{5} (<1)	b
	6/77	c	c	c	c	c	c	c	c
	7/77	3.2x10^{3} (10)	b	b	b	b	2.7x10^{4} (10)	b	b
	5/78	b	b	b	2.7x10^{5} (10)	b	b	1.9x10^{5} (10)	b
	10/79	b	b	b	2.1x10^{5} (10)	b	b	1.4x10^{5} (10)	1.9x10^{4} (10)
	10/81	b	3.2x10^{5} (<1)	b	2.4x10^{5} (<1)	1.9x10^{4} (<1)	b	2.9x10^{4} (<1)	b
Pu-238	9/76	3.7x10^{3} (2.7)	4.8x10^{0} (20)	5.7x10^{2} (5.9)	1.6x10^{5} (7.6)	b	3.0x10^{4} (6.8)	1.3x10^{4} (3.1)	b
	6/77	c	c	c	c	c	c	c	c
	7/77	9.1x10^{3} (10)	b	b	b	b	1.3x10^{5} (10)	b	b
	5/78	b	b	b	2.0x10^{5} (10)	b	b	4.0x10^{3} (10)	b
	10/79	b	b	b	7.2x10^{4} (6.0)	b	b	2.6x10^{4} (10)	2.0x10^{2} (10)
	10/81	b	9.3x10^{0} (32)	b	3.5x10^{5} (10)[d]	2.2x10^{4} (10)	b	9.0x10^{3} (12)[e]	b
Pu-239/240	9/76	4.1x10^{2} (8.6)	<1.0x10^{0}	5.1x10^{1} (20)	2.1x10^{4} (24)	b	2.7x10^{3} (2.2)	1.7x10^{3} (13)	b
	6/77	c	c	c	c	c	c	c	c
	7/77	2.9x10^{2} (10)	b	b	b	b	3.5x10^{3} (10)	b	b
	5/78	b	b	b	8.4x10^{2} (10)	b	b	6.7x10^{2} (10)	b
	10/79	b	b	b	2.6x10^{2} (6.0)	b	b	2.5x10^{3} (10)	3.3x10^{2} (10)
	10/81	b	2.6x10^{0} (72)	b	9.6x10^{2} (10)	6.9x10^{1} (14)	b	1.8x10^{2} (18)	b
Am-241	9/76	4.3x10^{3} (3.9)	<2.0x10^{1}	<2.0x10^{1}	7.7x10^{3} (7.0)	b	1.0x10^{3} (5.7)	1.5x10^{4} (3.8)	b
	6/77	4.7x10^{3} (6.2)	<6.7x10^{2}	<2.2x10^{2}	<2.8x10^{2}	<1.8x10^{2}	1.0x10^{3} (9.5)	2.7x10^{3} (10)	<2.8x10^{2}
	7/77	2.9x10^{3} (8.9)	b	b	b	b	c	b	b
	5/78	b	b	b	1.5x10^{3} (17)	b	b	1.4x10^{3} (17)	b
	10/79	b	b	b	1.3x10^{3} (15)	b	b	4.7x10^{3} (3.0)	1.2x10^{2} (22)
	10/81	b	3.9x10^{2} (25)	b	4.5x10^{4} (1.0)	1.4x10^{2} (20)	b	3.0x10^{2} (20)	b
Cs-134	9/76	<1.0x10^{2}	<1.0x10^{2}	<1.0x10^{2}	<1.0x10^{2}	b	5.6x10^{1} (18)	<1.0x10^{2}	b
	6/77	<1.7x10^{2}	<2.5x10^{2}	<1.6x10^{2}	<1.2x10^{2}	<1.1x10^{2}	1.6x10^{1} (29)	5.7x10^{2} (16)	<2.9x10^{2}
	7/77	c	b	b	b	b	c	b	b
	5/78	b	b	b	c	b	b	c	b
	10/79	b	b	b	c	b	b	c	2.2x10^{2} (9.6)
	10/81	b	1.0x10^{2} (40)	b	<5.0x10^{1}	<2.0x10^{1}	b	4.5x10^{1} (30)	b
Cs-137	9/76	<1.0x10^{2}	4.1x10^{3} (2.9)	4.4x10^{3} (3.0)	2.8x10^{3} (9.8)	b	6.7x10^{3} (20)	2.0x10^{4} (2.4)	b
	6/77	<2.3x10^{2}	3.0x10^{3} (12)	4.3x10^{3} (6.8)	4.2x10^{3} (5.2)	<1.6x10^{2}	4.0x10^{3} (2.0)	5.1x10^{3} (2.1)	8.3x10^{4} (1.1)
	7/77	c	b	b	b	b	4.8x10^{3} (5.7)	b	b
	5/78	b	b	b	9.0x10^{3} (3.8)	b	b	7.2x10^{3} (4.6)	b
	10/79	b	b	b	2.6x10^{3} (2.8)	b	b	2.1x10^{3} (3.2)	2.8x10^{4} (<1)
	10/81	b	1.0x10^{5} (1)	b	1.2x10^{4} (1)	3.2x10^{3} (1)	b	1.2x10^{4} (1)	b
Co-60	9/76	7.1x10^{4} (1.9)	1.3x10^{3} (5.1)	1.1x10^{4} (1.5)	6.6x10^{2} (23)	b	6.6x10^{3} (6.8)	1.0x10^{4} (3.2)	b
	6/77	1.1x10^{4} (3.1)	4.8x10^{4} (1.4)	1.3x10^{4} (2.8)	7.3x10^{3} (13)	<1.6x10^{2}	2.6x10^{2} (8.6)	7.3x10^{3} (1.4)	1.7x10^{4} (2.4)
	7/77	5.7x10^{3} (4.5)	b	b	b	b	8.0x10^{3} (14)	b	b
	5/78	b	b	b	1.6x10^{3} (11)	b	b	8.3x10^{2} (21)	b
	10/79	b	b	b	2.5x10^{3} (30)	b	b	3.1x10^{3} (2.6)	2.8x10^{4} (<1)
	10/81	b	1.6x10^{3} (3)	b	2.9x10^{4} (1)	1.5x10^{3} (1)	b	5.2x10^{3} (1)	b

[a] All concentrations, expressed as pCi/L, are decay corrected to October, 1981; the number in () represents 2σ% counting uncertainty.

[b] Not sampled.

[c] Not determined.

[d] Np-237 < 10 pCi/L in Trench 19W.

[e] Np-237 < 2.4 pCi/L in Trench 27.

Table 3.9. Radionuclide concentrations in trench leachates sampled during the period 1976-1981.[a](continued)

Radionuclide	Sampling Date	Trench 32	Trench 33L4	Trench 33L8	Trench 33L9	Trench 33L18	Trench 35	Trench 37
H-3	9/76	1.6x10^{8} (<1)	4.7x10^{7} (<1)	b	4.7x10^{7} (<1)	b	b	8.0x10^{6} (<1)
	6/77	1.5x10^{9} (<1)	4.6x10^{7} (1.3)	1.0x10^{6} (5.1)	2.0x10^{7} (1.3)	3.9x10^{7} (<1)	1.9x10^{9} (<1)	7.7x10^{6} (2.2)
	7/77	1.8x10^{9} (<1)	b	b	b	b	b	b
	5/78	b	2.4x10^{7} (<1)	b	b	3.8x10^{7} (<1)	b	b
	10/79	1.9x10^{9} (<1)	b	b	b	b	b	b
	10/81	b	4.4x10^{7} (3)	1.3x10^{7} (3)	b	b	5.5x10^{9}(1)	b
Sr-90	9/76	3.4x10^{5} (<1)	2.1x10^{4} (<1)	b	9.7x10^{3} (<1)	b	b	1.7x10^{3} (<1)
	6/77	c	c	c	c	c	c	c
	7/77	4.9x10^{5} (<10)	b	b	b	b	b	b
	5/78	b	1.6x10^{4} (10)	b	b	3.1x10^{4} (10)	b	b
	10/79	3.0x10^{5} (10)	b	b	b	b	b	b
	10/81	b	1.5x10^{4} (<1)	4.4x10^{2} (2)	b	b	1.5x10^{4} (<1)	b
Pu-238	9/76	3.5x10^{3} (4.2)	9.5x10^{3} (4.4)	b	b	b	b	1.7x10^{4} (1.0)
	6/77	c	c	c	c	c	c	c
	7/77	1.1x10^{5} (10)	b	b	b	b	b	b
	5/78	b	4.1x10^{2} (10)	b	b	7.7x10^{3} (12)	b	b
	10/79	3.6x10^{4} (10)	b	b	b	b	b	b
	10/81	b	4.3x10^{2} (10)	7.9x10^{0} (36)	b	b	5.1x10^{3} (10)	b
Pu-239/240	9/76	1.1x10^{2} (25)	8.4x10^{2} (40)	b	b	b	b	3.1x10^{2} (2.6)
	6/77	c	c	c	c	c	c	c
	7/77	2.9x10^{3} (10)	b	b	b	b	b	b
	5/78	b	6.6x10^{3} (10)	b	b	2.4x10^{3} (20)	b	b
	10/79	8.1x10^{2} (10)	b	b	b	b	b	b
	10/81	b	8.4x10^{3} (10)	1.2x10^{0} (100)	b	b	7.1x10^{1} (10)	b
Am-241	9/76	<4.0x10^{1}	<2.0x10^{1}	b	<4.0x10^{1}	b	b	2.8x10^{4} (1.0)
	6/77	<3.0x10^{2}	2.0x10^{2} (47)	<1.9x10^{2}	<1.7x10^{2}	4.7x10^{3} (10)	2.4x10^{2} (33)	9.3x10^{3} (4)
	7/77	c	b	b	b	b	b	b
	5/78	b	c	b	b	3.9x10^{3} (5.8)	b	b
	10/79	6.0x10^{3} (3.0)	b	b	b	b	b	b
	10/81	b	<4.0x10^{1}	<3.0x10^{1}	b	b	4.4x10^{2} (8)	b
Cs-134	9/76	7.6x10^{1} (24)	<1.0x10^{2}	b	<1.0x10^{2}	b	b	3.1x10^{2} (4.3)
	6/77	<1.6x10^{2}	<1.0x10^{2}	<1.7x10^{2}	<1.4x10^{2}	6.1x10^{2} (12)	<1.7x10^{2}	1.9x10^{2} (46)
	7/77	c	b	b	b	b	b	b
	5/78	b	c	b	b	1.2x10^{3} (14)	b	b
	10/79	3.5x10^{1} (23)	b	b	b	b	b	b
	10/81	b	<4.0x10^{1}	<2.0x10^{1}	b	b	1.2x10^{2} (9)	b
Cs-137	9/76	5.3x10^{3} (4.6)	<1.0x10^{2}	b	4.3x10^{3} (5.3)	b	b	8.7x10^{3} (2.1)
	6/77	3.8x10^{3} (5.7)	<2.0x10^{1}	<2.0x10^{2}	2.5x10^{3} (7.6)	3.2x10^{4} (1.8)	4.1x10^{2} (12)	3.7x10^{3} (6.9)
	7/77	4.3x10^{3} (5.5)	b	b	b	b	b	b
	5/78	b	1.9x10^{2} (66)	b	b	2.0x10^{4} (2.4)	b	b
	10/79	3.1x10^{3} (2.4)	b	b	b	b	b	b
	10/81	b	<6.0x10^{1}	8.9x10^{1} (10)	b	b	1.0x10^{4} (1)	b
Co-60	9/76	3.1x10^{3} (5.6)	<3.0x10^{2}	b	1.6x10^{3} (9.0)	b	b	2.6x10^{4} (1.0)
	6/77	1.2x10^{3} (13)	<1.8x10^{2}	3.1x10^{3} (2.2)	1.1x10^{3} (13)	4.3x10^{3} (5.0)	<2.9x10^{2}	2.0x10^{4} (2.2)
	7/77	2.0x10^{3} (8.1)	b	b	b	b	b	b
	5/78	b	2.3x10^{1} (64)	b	b	3.5x10^{3} (6.6)	b	b
	10/79	1.8x10^{3} (3.6)	b	b	b	b	b	b
	10/81	b	1.4x10^{1} (10)	1.4x10^{2} (8)	b	b	1.5x10^{2} (9)	b

[a] All concentrations, expressed as pCi/L, are decay corrected to October, 1981; the number in () represents 2σ % counting uncertainty.

[b] Not sampled.

[c] Not determined.

Table 3.10. Average radionuclide concentrations in trench leachates sampled during the period 1976-1981.

	Concentration[a]							
Trench	H-3	Sr-90	Pu-238	Pu-239,240	Am-241	Cs-134	Cs-137	Co-60
2	$1.7x10^{7}$	$4.6x10^{3}$	$6.4x10^{3}$	$3.5x10^{2}$	$4.0x10^{3}$	$<1.0x10^{2}$	$<1.0x10^{2}$	$7.9x10^{3}$
7	$3.0x10^{8}$	$1.1x10^{6}$	$7.1x10^{0}$	$2.6x10^{0}$	$3.9x10^{2}$	$1.0x10^{2}$	$3.6x10^{4}$	$1.7x10^{4}$
18	$3.4x10^{8}$	$4.7x10^{4}$	$5.7x10^{2}$	$5.1x10^{1}$	$<2.0x10^{1}$	$<1.0x10^{2}$	$4.8x10^{3}$	$1.2x10^{4}$
19s	$7.0x10^{7}$	$2.4x10^{5}$	$2.0x10^{5}$	$5.8x10^{3}$	$1.4x10^{4}$	$<5.0x10^{1}$	$6.1x10^{3}$	$6.9x10^{3}$
23	$1.0x10^{9}$	$1.9x10^{4}$	$2.2x10^{4}$	$6.9x10^{1}$	$1.4x10^{2}$	$<2.0x10^{1}$	$3.2x10^{3}$	$1.5x10^{3}$
26	$1.1x10^{8}$	$2.9x10^{4}$	$8.0x10^{4}$	$3.1x10^{3}$	$1.0x10^{3}$	$3.6x10^{1}$	$5.2x10^{3}$	$5.7x10^{2}$
27	$2.3x10^{9}$	$1.4x10^{5}$	$1.3x10^{4}$	$1.3x10^{3}$	$4.8x10^{3}$	$7.6x10^{1}$	$9.3x10^{3}$	$5.3x10^{3}$
30	$1.1x10^{10}$	$1.9x10^{4}$	$2.0x10^{2}$	$3.3x10^{2}$	$1.2x10^{2}$	$2.2x10^{2}$	$5.6x10^{4}$	$2.2x10^{4}$
32	$1.3x10^{9}$	$3.8x10^{5}$	$5.0x10^{4}$	$1.3x10^{3}$	$6.0x10^{3}$	$5.6x10^{1}$	$4.1x10^{3}$	$2.0x10^{3}$
33L4	$4.0x10^{7}$	$1.7x10^{4}$	$3.5x10^{3}$	$5.3x10^{3}$	$2.0x10^{2}$	$<4.0x10^{1}$	$1.9x10^{2}$	$1.8x10^{1}$
33L8	$7.0x10^{6}$	$4.4x10^{2}$	$7.9x10^{0}$	$1.2x10^{0}$	$<3.0x10^{1}$	$<2.0x10^{1}$	$1.4x10^{2}$	$1.6x10^{3}$
33L9	$3.3x10^{7}$	$9.7x10^{3}$	b	b	$<4.0x10^{1}$	$<1.0x10^{1}$	$3.4x10^{3}$	$1.4x10^{4}$
33L18	$3.8x10^{7}$	$3.1x10^{4}$	$7.7x10^{3}$	$2.4x10^{3}$	$4.3x10^{3}$	$6.4x10^{2}$	$2.6x10^{4}$	$4.1x10^{3}$
35	$3.7x10^{9}$	$1.5x10^{4}$	$5.1x10^{3}$	$7.1x10^{1}$	$3.4x10^{2}$	$1.2x10^{2}$	$5.2x10^{3}$	$1.5x10^{2}$
37	$7.8x10^{6}$	$1.7x10^{3}$	$1.7x10^{4}$	$3.1x10^{2}$	$1.9x10^{4}$	$2.5x10^{2}$	$6.2x10^{3}$	$2.3x10^{4}$

[a] All concentrations, expressed as pCi/L, are decay corrected to October 1981.

[b] Not determined.

Am-241 concentrations range from below detection in leachates 18, 33L8, and 33L9 to a high of ≈10^{4} pCi/L in leachates 19s and 37.

As reported in the survey study, Cs-134 is below the limits of detection in many leachates. The highest concentration, at a level of 6.4×10^{2} pCi/L, was observed in leachate 33L18, which also shows significant enrichment of Cs-137.

3.7 Total Dissolved Carbon and Organic Compounds

Water samples collected from several trenches were analyzed for total dissolved carbon and for both hydrophobic and hydrophilic organic constituents.

The concentrations of total dissolved carbon, inorganic carbon, and organic carbon in the various trench leachates are given in Table 3.11. The total dissolved carbon concentrations range from a low of 460 mg/L in leachates 7(76) to a high of 3300 mg/L in leachates 37(76). In most leachates, the dissolved organic carbon represents a major fraction of the total dissolved carbon, while in several cases the dissolved organic carbon accounts for the total amount of carbon dissolved in the leachates. The highest dissolved organic carbon concentration (3280 mg/L) is observed in leachate 37(76). Relative to dissolved organic carbon concentrations, the inorganic carbon present in solution is low in most cases. The highest concentration (1500 mg/L) is observed in leachate 30(79) which also exhibits a relatively low concentration of dissolved organic carbon. In leachates 27(76,78) and 33L4(81), the dissolved inorganic carbon concentrations were found to below the detection limit of 2 ppm.

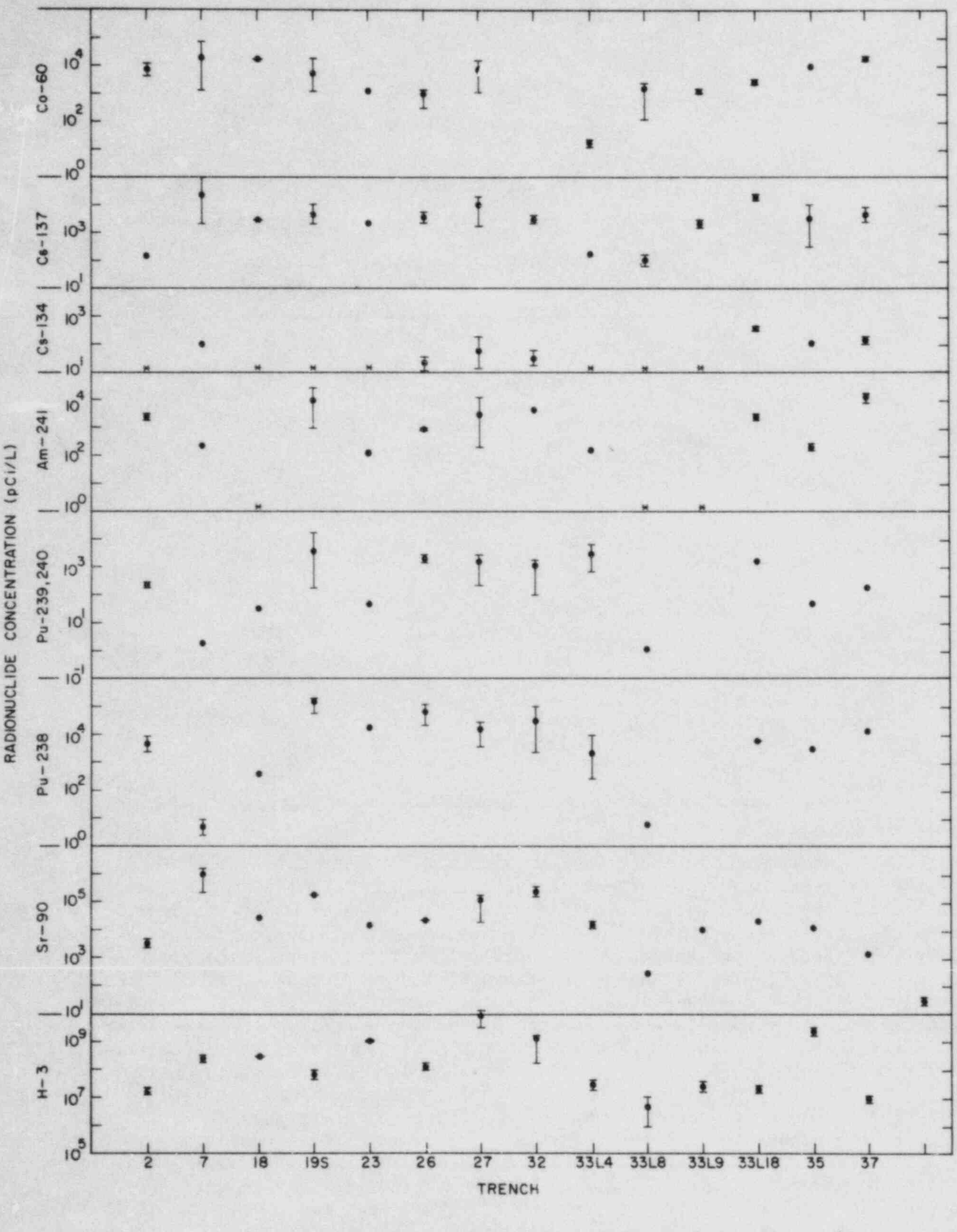


Figure 3.5. Average radionuclide concentrations in trench leachates (decay corrected to October 1981) based on multiple samplings during the period 1976-1981. The error bars represent the extent of variation observed in radionuclide concentrations in a given trench sampled multiply. Asterisk (*) indicates concentrations below detection limits.

Table 3.11. Dissolved carbon concentrations in trench leachates.

Sample	Dissolved Carbon (mg/L) Total	Inorganic	Organic
2(76)	480	270	210
7(76)	460	210	250
7(81)	950	220	730
18(76)	940	440	500
19s(76)	700	80	620
19s(81)	600	170	430
23(81)	1300	520	780
26(76)	1100	150	950
27(76)	730	<2	730
27(78)	540	<2	540
27(79)	1574	74	1500
27(Av)	948	25	923
27(81)	550	57	493
30(79)	1760	1500	260
32(76)	1300	510	790
33L4(78)	1110	10	1100
33L4(81)	1500	<2	1500
33L8(81)	490	330	160
35(81)	930	390	540
37(76)	3300	20	3280

The hydrophobic organic compounds reported in Table 3.12 are those found in the methylene chloride extract of selected leachate samples. The hydrophobic organic constituents identified in the leachates consist of several straight- and branched-chain aliphatic acids, aromatic acids, alcohols, aldehydes, ketones, amines, aromatic hydrocarbons, esters, ethers, phenols, and heterocyclics. Table 3.12 shows the range of concentrations observed for the various hydrophobic organic compounds in the trench leachates. The total concentrations of hydrophobic constituents range from 6 mg/L in leachate 30(79) to a high of 78 mg/L in leachate 32(76). In most leachates, the carboxylic acids represent a major fraction of the total hydrophobic constituents.

The hydrophilic organic compounds are those which are present in the non-extractable methylene chloride fraction. The hydrophilic organic groups of compounds identified consist of chelating agents, dicarboxylic acids, and phthalate esters. A detailed listing of the various carboxylic acids and phthalates observed is given in Table 3.13. The total concentrations of hydrophilic constituents range from less than 1 mg/L in 33L8(81) to a high of 31 mg/L in 23(81). The chelating agents represent a major fraction of the total hydrophilic constituents, except in leachates 7(81) and 35(81) where the phthalate esters dominate. Leachates 33L4(81) and 33L8(81) are predominantly enriched in dicarboxylic acids, representing a major fraction of the total hydrophilic constituents.

Table 3.12. Hydrophobic organic compounds in selected trench leachates.[a,b]

	Trench Leachates[c,d]								
Hydrophobic Organic Compounds	19s(76)	19s(79)	26(76)	27(76)	27(79)	30(79)	32(76)	32(79)	33L4(78)
Carboxylic acids	25	6.9	42	22	14	5.6	64	7.9	35
Benzoic acid	0.22		1.2	0.22	0.24		1.9		0.59
C6 acids	0.35	0.26		0.66	0.16	1.8			1.1
C8 acids	1.4	2.1		d	0.14	d		0.80	
2-Ethylhexanoic acid	5.6	1.9	3.4	17	9.7	1.1	8.8	3.2	27
Hexanoic acid	1.5		1.9	1.2	0.64		4.7		2.0
Isobutyric acid							2.0		
2-Methylbutanoic acid	4.6	0.52	19	0.98	0.60		13		
3-Methylbutanoic acid	1.8	0.80		0.48	0.76		5.8		1.6
2-Methylhexanoic acid	1.5	0.13	1.2	0.40	0.24		3.2	0.57	0.30
2-Methylpentanoic acid			4.2		0.45		4.0		
3-Methylpentanoic acid	3.1	0.67	3.6				1.4	0.98	
2-Methylpropionic acid	0.40	0.12			0.24				
Nonanoic acid		0.08							
Octanoic acid	0.36			0.64	0.10		1.3	0.20	0.39
Pentanoic acid			4.6				4.7		
Phenylacetic acid	0.56	0.34	1.5	0.08	0.16		3.4		0.25
Phenylhexanoic acid	d	d		d	d		d	d	
Phenylpropionic acid	1.2		1.3	0.56	0.50		9.8		0.70
Toluic acid						2.7		2.1	
Valeric acid	2.0				0.28				1.3
Esters	0.54	0.45			0.29		0.36	0.30	
Triethyl phosphate	0.38	0.18		d	0.29				
Tributyl phosphate	0.16	0.17					0.36	0.30	
Hydrocarbons	3.0	9.6	3.8	3.6	0.62		7.8	2.6	0.39
Alkanes (C10-C31)									
Dimethyl naphthalene									
Naphthalene	0.12	0.03	0.28	0.15	0.06		0.28	0.07	
Toluene	2.9	9.5	3.5	3.4	0.56		7.0	2.4	0.39
Xylene	d	0.03					0.48	0.13	
Alcohols	2.9	0.10	0.31	0.23	0.19		0.73		1.1
Cyclohexanol	2.9	0.10					0.24		1.1
Diethylene glycol		d			d				
Ethylene glycol		d			d	d	d		
2-Ethyl-1-Hexanol				0.23	0.17				d
α-Terpineol			0.31				0.49		
Phenols	2.9	1.2	2.0	1.1	0.79		5.4	0.36	9.1
Cresol isomers	2.9	1.2	2.0	0.70	0.56		4.2	0.28	0.28
Phenol		0.04		0.40	0.23		1.2	0.08	0.20
Vanillan									8.6
Ketones and Aldehydes	0.59	0.20			1.8	0.08			1.1
Camphor	d			d	d				
Cyclohexanone									1.1
Dibutylketone	d	d							
Fenchone	0.03			d	d	0.08			
Methylisobutyl ketone	0.56	0.20			1.8				
Total	34	19	48	27	18	6	78	11	47

[a] All concentrations are reported in mg/L.

[b] Results of trench leachates 2(76), 7(76), 18(76), 37(76) and well water UB1A(79) are reported elsewhere (Weiss and Colombo, 1980). However, qualitative analysis revealed the presence of similar hydrophobic organic constituents in those leachates.

[c] PNL identified several heterocyclic hydrophobic compounds in leachates 7(81), 19s(81,82), 23(81), 27(81,82) and 35(81). The following compounds were reported: Barbital, Benzofuran, Benzothiazol, 2(3H) bensothiazalone, caffeine, caprolactam, 1,3-dihydro-2H-indol-2-one, p-dioxane, nicotine, pentabarbital, piperidinone, and tetrahydrofuran. Detailed analysis of leachate 27(4/81) revealed the presence of several hydrocarbon and hydrocarbon halide classes of compounds. Further details are given elsewhere (Kirby et al., 1984).

[d] Compounds were identified but not quantified; blank spaces indicate compounds not detected.

Table 3.13. Hydrophilic organic compounds in selected trench leachates[a,b]

Hydrophilic Organic Compounds	Trench Leachates						
	7(81)	19s(81)	23(81)	27(78)	33L4(81)	33L8(81)	35(81)
Chelating agents	6.2	23	28	1.2	0.40	0.08	0.87
Ethylenediaminetetraacetic acid (EDTA)	5.01	12.4	4.89	0.96	0.40	0.078	0.868
N-Hydroxyethylethylenediaminetriacetic acid (HEDTA)		8.35	19.5				
Ethylenediaminetriacetic acid (ED3A)	1.19	2.19	3.88	0.212			
Dicarboxylic acids	2.8	0.56	0.45	0.35	2.6	0.39	2.2
Oxalic acid							
Succinic acid	0.345			0.026		0.039	0.080
Methylsuccinic acid	0.191			0.021		0.021	0.231
Pentanedioic acid	0.248			0.041		0.054	0.406
Hexanedioic acid	1.57	0.223	0.244	0.167	0.451	0.104	0.834
Methylhexanedioic acid							0.305
Octanedioic acid					0.781	0.057	
Nonanedioic acid	0.455	0.338	0.210	0.096	1.39	0.111	0.314
Monocarboxylic acids					0.03	0.172	
Dodecanoic acid							
Hexadecanoic acid						0.061	
Nondnoic acid							
Octadecanoic acid					0.031	0.111	
Oxygenated acids	2.2			0.03		0.04	0.19
Citric acid							
4-Oxo-Pentanoic acid	2.7			0.029		0.043	0.185
Aromatic acids	1.9	0.44	0.90	0.08		0.03	2.0
Benzoic acid							
2-Hydroxybenzoic acid						0.027	
1,3-Benzenedicarboxylic acid	0.381	0.276	0.440	0.077			0.877
1,4-Benzenedicarboxylic acid	1.18	0.162	0.457				1.14
1,2,4-Benzenetricarboxylic acid	0.311						
Pentafluorobenzoic acid							
Phthalate esters	8.8	3.05	1.8	1.3		0.10	14
Dibutyl phthalate							
Dimethyl phthalate	8.82	2.836	1.67	0.391		0.098	13.6
Methyl phthalate		0.213	0.108	0.012			0.874
Dioctyl phthalate				0.851			
Total	22	27	31	3.0	3.0	0.81	19

[a] Concentrations reported in mg/L; methylated (BF_3/Methanol) acids identified as methyl esters; analysis conducted by PNL; samples collected by BNL.

[b] No entry indicates compound is below detection levels.

A comparison of the concentrations of hydrophilic and hydrophobic constituents and total dissolved organic carbon is shown in Figure 3.6. The hydrophilic constituents represented are total chelating agents, total carboxylic acids (dicarboxylic acids, monocarboxylic acids, oxygenated acids, and aromatic acids), and phthalate esters observed in the various trench leachates. The hydrophobic constituents, displayed in Figure 3.6, indicate that the concentration ranges for the total hydrophilic and hydrophobic constituents observed in the various trench leachates are comparable and that they are significantly lower (two or three orders of magnitude) than the total dissolved organic carbon in the leachates. This observation indicates that a large fraction of the total dissolved organic carbon has not been characterized and most probably consists of high molecular weight organic compounds such as humic and fulvic acids.

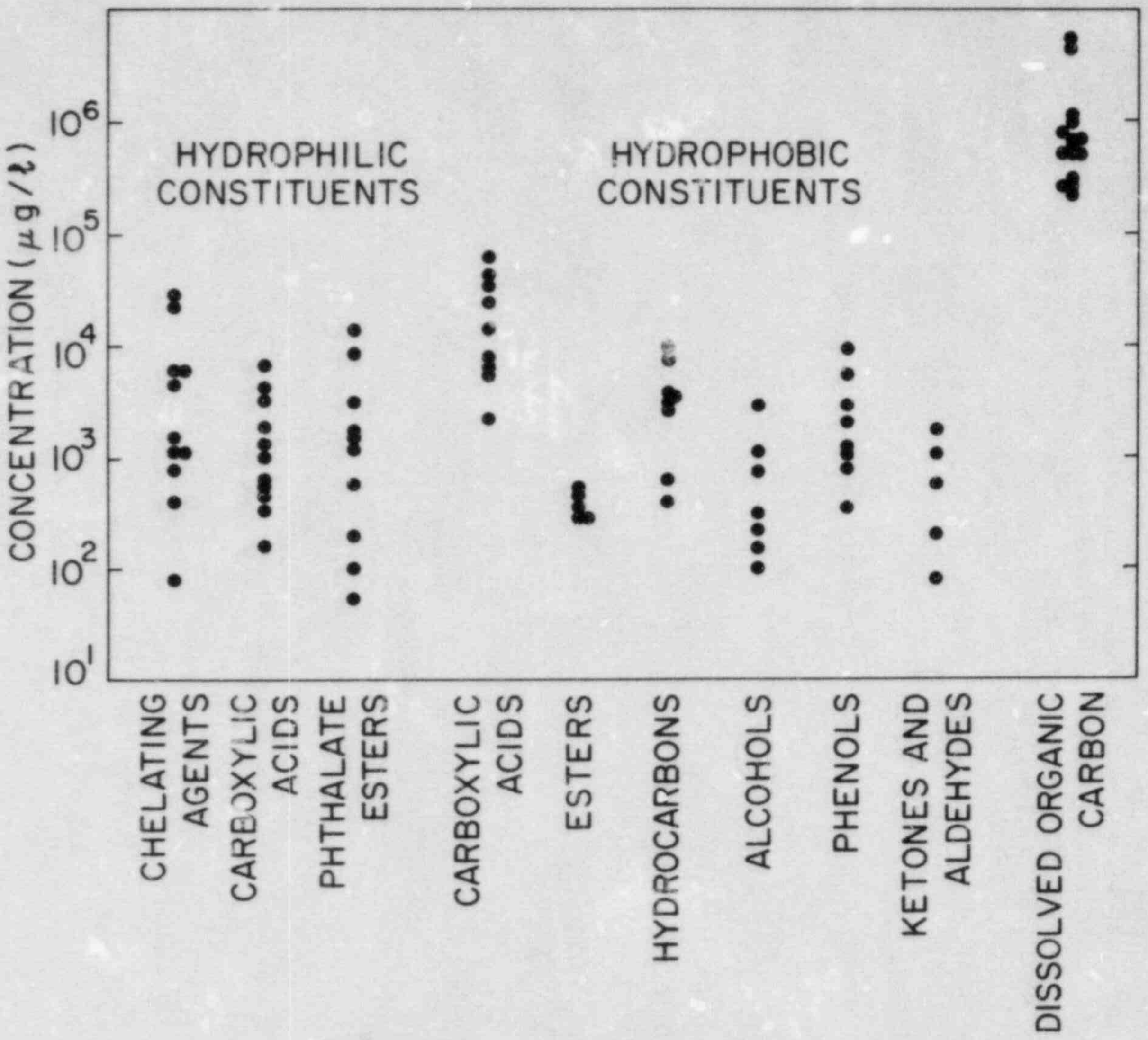


Figure 3.6. Comparison of the concentration ranges for hydrophilic and hydrophobic constituents observed in the various trench leachates. The range of total dissolved organic carbon concentrations are also presented.

4. DISCUSSION

4.1 Leachate Formation and Anoxia in Trenches

The combination of hydrological and geochemical factors determine to a large extent the nature and amount of leachate produced in a trench at a given site. At the Maxey Flats site, the waste trenches are located in non-porous shale of relatively low hydraulic conductivity. Consequently, this leads to accumulation of rainwater that infiltrates through the trench caps. Such stagnant accumulations of water and eventual overflow at the Maxey Flats site has been termed the "Bathtub Effect". Because of the long residence time of accumulated water in the trenches, prolonged leaching and microbial degradation of buried waste materials occurs and leads to leachate formation. As a result of such interactions for extended time periods, the resultant trench leachates acquire geochemical properties which are unique compared to natural groundwater. The important biogeochemical processes controlling the formation and composition of trench leachates are discussed in the following sections.

4.1.1. Microbial Degradation of Organic Wastes

The development of anoxia can be attributed to redox conditions in trench leachates largely controlled by microbial degradation of organic matter present in the buried wastes. A large fraction of wastes buried in the trenches consists of unconsolidated organic materials. Many components of these materials are subject to both aerobic and anaerobic microbial degradation processes. The presence of aerobic and anaerobic sulphate reducing, denitrifying, and methanogenic bacteria have been reported in the trench leachates and these bacteria are able to grow anaerobically (Weiss and Colombo, 1980).

Given the relatively stagnant leachate accumulations in the trenches at Maxey Flats, the dissolved oxygen is consumed rapidly during aerobic decomposition processes. Following depletion of all molecular oxygen, further degradation of organic material occurs by anaerobic processes which represent progressively lower Eh values as shown in Figure 4.1. As discussed below, the anaerobic degradation of organic matter involves denitrification, followed successively by sulphate reduction and methane generation. During these aerobic and anaerobic oxidation processes, there is a continual production and buildup of decomposition products such as carbon dioxide and ammonia which causes the alkalinity, total aqueous CO_2, and ammonia contents of the trench leachates to increase. Concurrently, dissolved oxygen, sulphate, and nitrate are consumed, resulting in negative redox potentials and the presence of sulphide in solution. Iron reduction contributes to high concentrations of dissolved iron, present primarily as Fe^{2+} (Aller, 1983; Dayal et al., 1983).

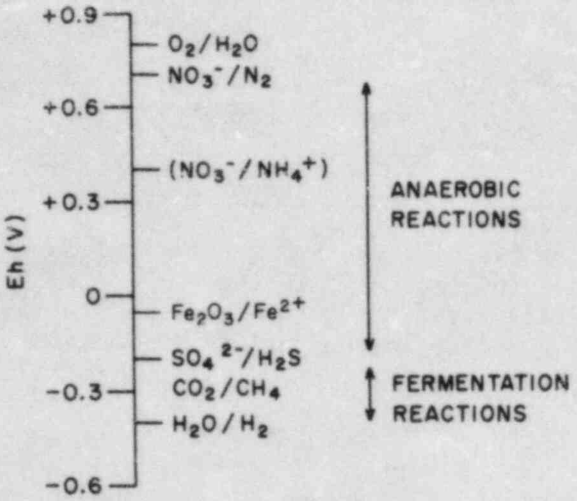


Figure 4.1. Approximate Eh values at which various redox reactions occur in water at pH 7 and 25°C (after Drever, 1982).

Anaerobic oxidation of organic matter occurs in the following sequence:

(a) Denitrification

$$2.5C_{org} + 2NO_3^- + 2H^+ = N_2 + 2.5CO_2 + H_2O \qquad (4.1)$$

This is not an important process in that nitrate levels are low in most groundwaters. However, at Maxey Flats some trench leachates contain waste-derived nitrate. Particularly, in these trenches, denitrification could be important.

(b) Deamination of Amino Acids. Amino acids, which are constituents of protein, are decomposed under anaerobic condtions as follows

$$[\text{Amino Acid}] = [\text{N-free compounds}] + NH_3 \qquad (4.2)$$

The ammonia reacts to form NH_4^+,

$$NH_3 + H_2O + CO_2 = NH_4^+ + HCO_3^- \qquad (4.3)$$

(c) Sulphate reduction. The oxygen in the sulphate is used by bacteria to oxidize organic matter to CO_2, producing sulphide species as a by-product.

$$SO_4^{2-} + 2C_{org} + 2H_2O = H_2S + 2HCO_3^- \qquad (4.4)$$

HS^- will form rather than H_2S if the pH is >7 in pH units. Sulphate reduction is an important process in trench leachates.

(d) Fermentation reactions. There are many fermentation reactions, but the simplest fermentation reaction known to occur in some trench leachates at the Maxey Flats site is methane generation,

$$C_{org} + 2H_2O = CO_2 + CH_4 \qquad (4.5)$$

Methane generation fermentation reaction represents an advanced stage of microbial oxidation of organic matter, following sulphate depletion, and drives the redox potential to lower Eh values.

4.1.1.1. Redox Equilibria and Buffering in Trench Leachates

Although Eh measurements reflect the redox levels of aqueous systems, it is important to know which redox processes control and buffer the system. A redox buffered system is one in which reducible or oxidizable constituents are present that prevent changes in Eh in response to additions of small amounts of strong oxidizing or reducing agents (Drever, 1982). Figure 4.2 shows the change in Eh upon decomposition of organic matter in fresh water containing sedimentary material. In the absence of solid phases such as Mn and Fe oxides, there is a sharp drop in Eh to a constant value controlled by SO_4^{2-}/H_2S, following complete depletion of all molecular oxygen. The Eh value remains constant until all the dissolved sulphate is consumed by the process of bacterial sulphate reducton, at which point the fermentation reactions take over, as reflected by a steady decrease in Eh with further decomposition of organic matter. If the nitrate content of groundwaters is appreciable, reactions involving nitrogenous compounds such as denitrification (NO_3^-/NH_4^+) may provide some buffering between the O_2/H_2O and SO_4^{2-}/H_2S redox levels.

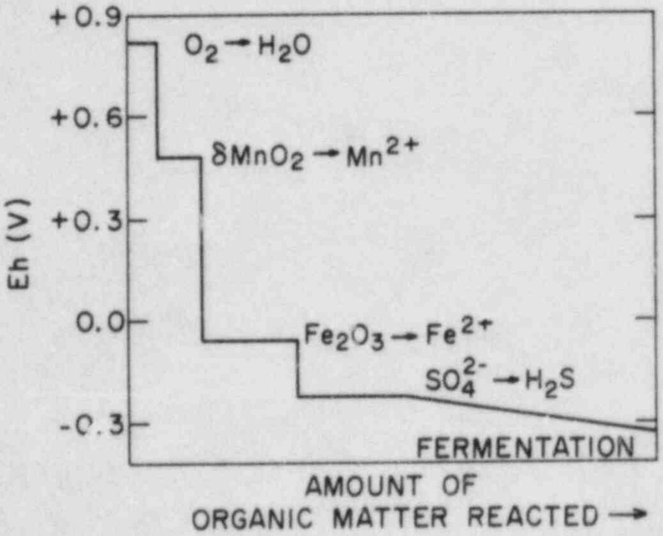


Figure 4.2. Redox sequence based on decomposition of organic matter in fresh water containing sedimentary matter (after Drever, 1982). The lengths of the horizontal segments are arbitrary, depending on the quantity and reactivity of specific solid phases. pH is assumed to remain constant at 7.0. Because of the initially low nitrate concentrations in groundwater, denitrification is assumed not to be an important redox process.

In the presence of iron and manganese oxides, reactions involving reduction of the solid oxide phases also provide buffering between the O_2/H_2O and SO_4^{2-}/H_2S pairs in the redox sequence (Figure 4.2).

In the discussion above, we have only evaluated redox buffers for relatively uncontaminated systems involving organic matter and solutes in the absence and presence of sedimentary material such as iron and manganese oxides. Cosidering the complexity of the solid phases and solute chemistry of the trench leachates, it is difficult to establish unambiguously the dominant redox buffers controlling the redox conditions in the trenches. However, plotting the leachate data on an Eh-pH diagram showing the various solid/solution boundaries representing the important redox buffers in a groundwater system (Figure 4.3), indicates that the redox levels of most leachates (region A) correspond to buffering by the Fe_2O_3/Fe^{2+} and SO_4^{2-}/H_2S pairs, reflecting the presence of reactive organic matter and relatively long residence times for infiltrated water in the trenches. In contrast, the ambient groundwater plots in region B which appears to be buffered by iron reduction [$(Fe(OH)_3/Fe^{2+}$ pair], indicating the absence of metabolizable organic matter in groundwater or that its residence time is relatively short.

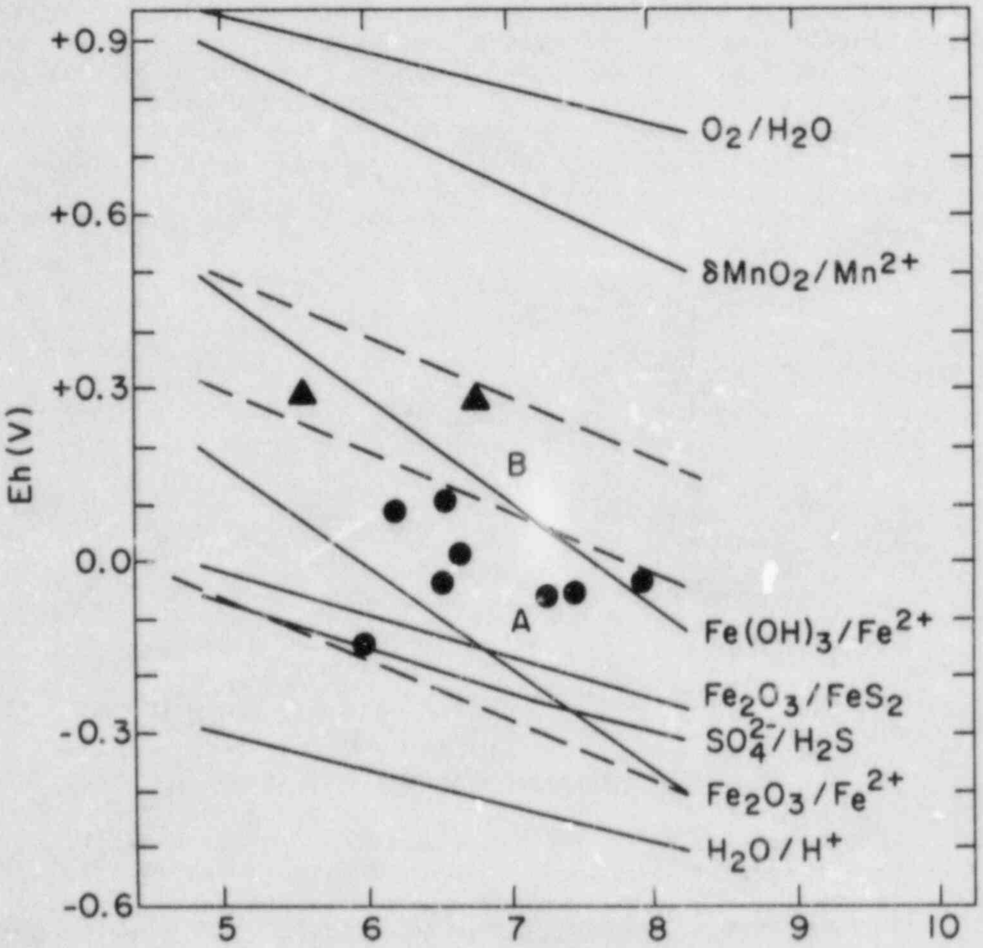


Figure 4.3. Solid/solution boundaries showing the various redox buffers in a groundwater system. Dashed lines delineate regions A and B showing the redox ranges for trench leachates (●) and groundwater (▲), respectively (Adapted from Drever, 1982).

It has been reported that, in complex aqueous systems, the measured redox potential often represents a mixed potential and does not respond to a particular redox couple (Jackson and Patterson, 1982, Stumm and Morgan, 1981). Assuming the SO_4^{2-}/H_2S and Fe_2O_3/Fe^{2+} redox buffers to be controlling the redox levels of the trench leachates and knowing the sulphate, bisulphide, and ferrous iron activities and the pH, we have obtained two sets of data, representing estimates of the redox potentials of trench leachates based on the two redox buffers. Our calculations show that the calculated redox potentials are consistently lower than the measured values for most trench leachates and that the estimated values still lie in region A (Figure 4.3). The calculated redox potentials appear to be more reflective of the redox conditions in that complete sulphate depletion and some generation of methane was observed in some of the trenches.

In summary, consideration of redox processes and leachate Eh and pH data indicate that Fe_2O_3/Fe^{2+} and SO_4^{2-}/H_2S pairs appear to be the dominant buffers controlling the redox conditions of most trench leachates.

4.1.1.2. Microbially Mediated Changes in Solute Chemistry

The enrichment and depletion of leachate constituents, relative to ambient groundwater, as a result of microbial degradation of organic wastes are given in Table 4.1. Figure 4.4 shows that the redox potentials for most leachates lie in the 0 to -100 mV range. Leachates 2(76), 26(76), and 30(79) have redox potentials around +100 mV. However, relative to the groundwater redox conditions ($\approx$+280 mV), all leachates exhibit redox potentials which are significantly lower, indicating chemically reducing conditions.

Relative to ambient groundwater comcentration, all leachates are significantly enriched in ammonium (Figure 4.5). As shown in Table 4.1, enrichments of as high as 120-fold are observed in leachate 27(81). The minimum enrichment (18x) is observed in leachate 33L4(78). As discussed earlier, the elevated levels of ammonium in the leachates can be attributed to its continual production and build up during the aerobic and anaerobic oxidation of organic waste materials.

Following complete oxygen depletion, bacterial sulphate reduction is an important process during anaerobic microbial degradation of organic matter. Figure 4.6 shows that, except for leachate 37(76), all trench leachates are significantly depleted in SO_4^{2-} relative to ambient groundwater. Leachates 19s(81), 27(81), 32(76), 33L4(81), and 35(81) exhibit the maximum depletion ($\approx 10^{-3}$). The least depletion of SO_4^{2-} is observed in leachate 7(81) (Table 4.1). Anomalously high concentration of SO_4^{2-} is observed in leachate 37(76) which could be waste-derived.

Table 4.1. Enrichment and depletion of leachate constituents due to biodegradation.

Leachate	Enrichment/Depletion Factors[a]		
	Alkalinity	$SO_4{}^{2-}$	$NH_4{}^{+b}$
	(x 10^0)	(x 10^{-3})	(x 10^1)
2 (76)	3.4	5.2	c
7 (76)	2.4	5.0[d]	c
7 (81)	2.5	0.06	7.5
18 (76)	4.5	8.6	c
19s (76)	2.1	5.0[d]	c
19s (81)	2.3	1.0	4.5
23 (81)	5.3	0.3	10
26 (76)	2.9	5.0[d]	c
27 (Av)	0.8	1.0	7.0
27 (81)	0.7	1.0[d]	12
30 (79)	14	0.4	5.0
32 (76)	5.9	1.0[d]	c
33L4 (78)	3.5	2.0	1.8
33L4 (81)	4.6	7.0	2.6
33L8 (81)	2.4	7.0[d]	5.0
35 (81)	5.0	1.0	3.7
37 (76)	0.3	3809	c

[a] Enrichment/Depletion Factor = C_t/C_w, where C_t represents concentration of species in trench leachate and C_w, the average well water concentration as reported by Zehner (1983) for well UA3.

[b] Since C_w was not available for these species in well water UA3, well water UB1A concentrations were used instead for calculating enrichment factors.

[c] Leachate not analyzed for ammonium.

[d] Detection limits of species in leachate were used to calculate enrichment and depletion factors.

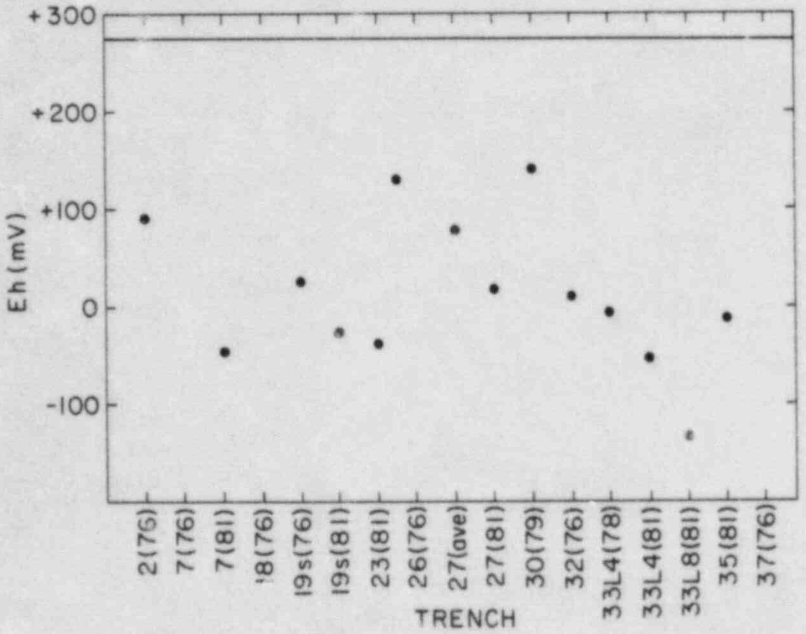


Figure 4.4. Redox potentials of trench leachates relative to ambient groundwater (solid line).

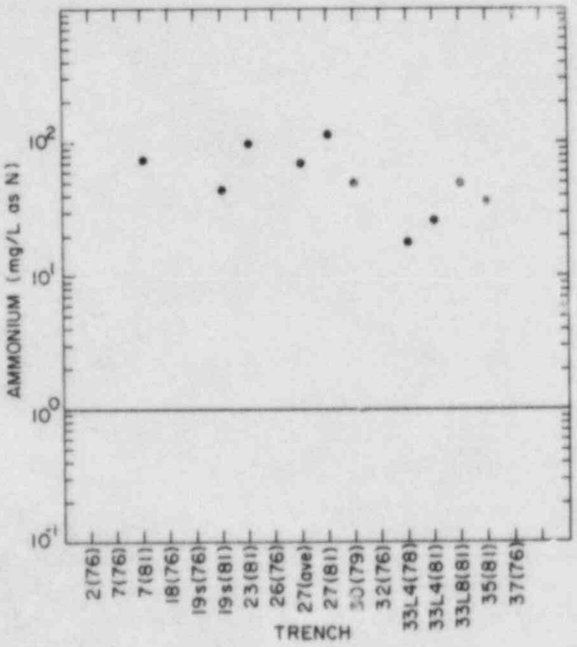


Figure 4.5. Ammonium concentrations in trench leachates relative to ambient groundwater (solid line).

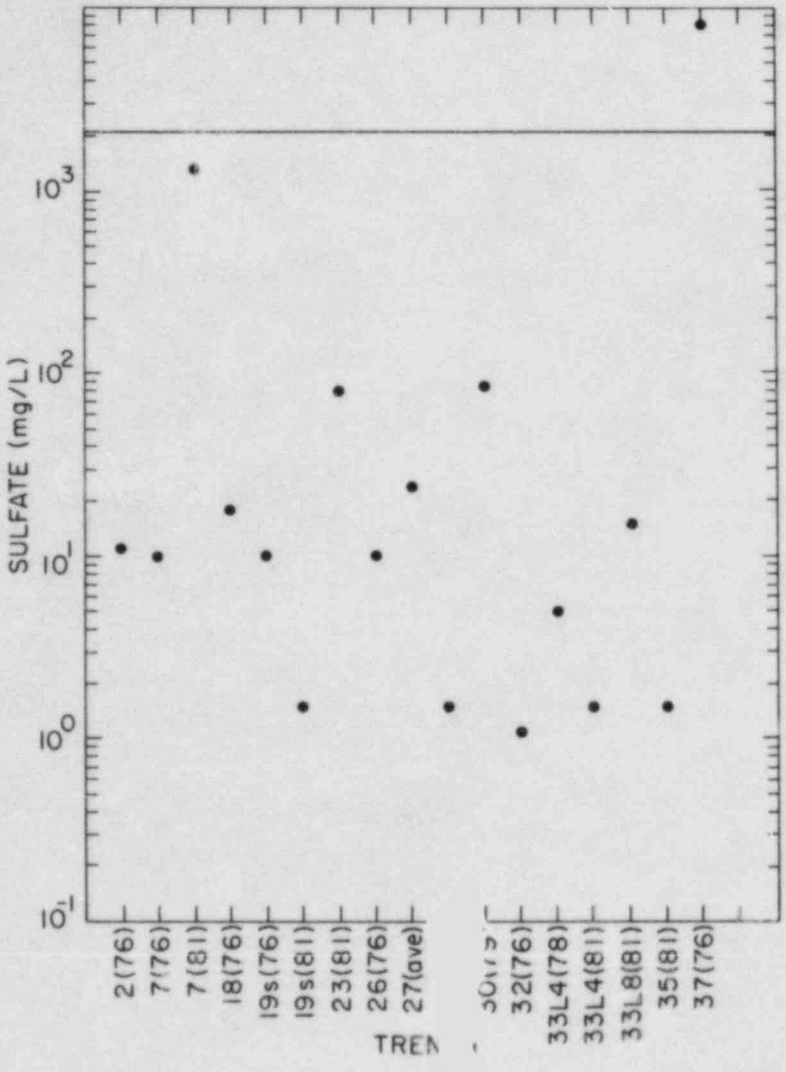


Figure 4.6. Sulphate concentrations in trench [illegible]achates relative to ambient groundwater (solid line).

The alkalinity plot in Figure 4.7 shows the magnitude of titratable components in trench leachates compared to that in ambient groundwater. For the sake of simplicity, we have assumed that carbonate alkalinity accounts for all the observed titration alkalinity in the leachates. Relative to groundwater, most leachates exhibit significant enrichment in alkalinity by factors of ≈2.5 for leachates 7(76,81), 19s(76,81), and 33L8(81) and 14 for 30(79) (Table 4.1). Leachate 37(76), however, shows depletion in alkalinity by a factor of three.

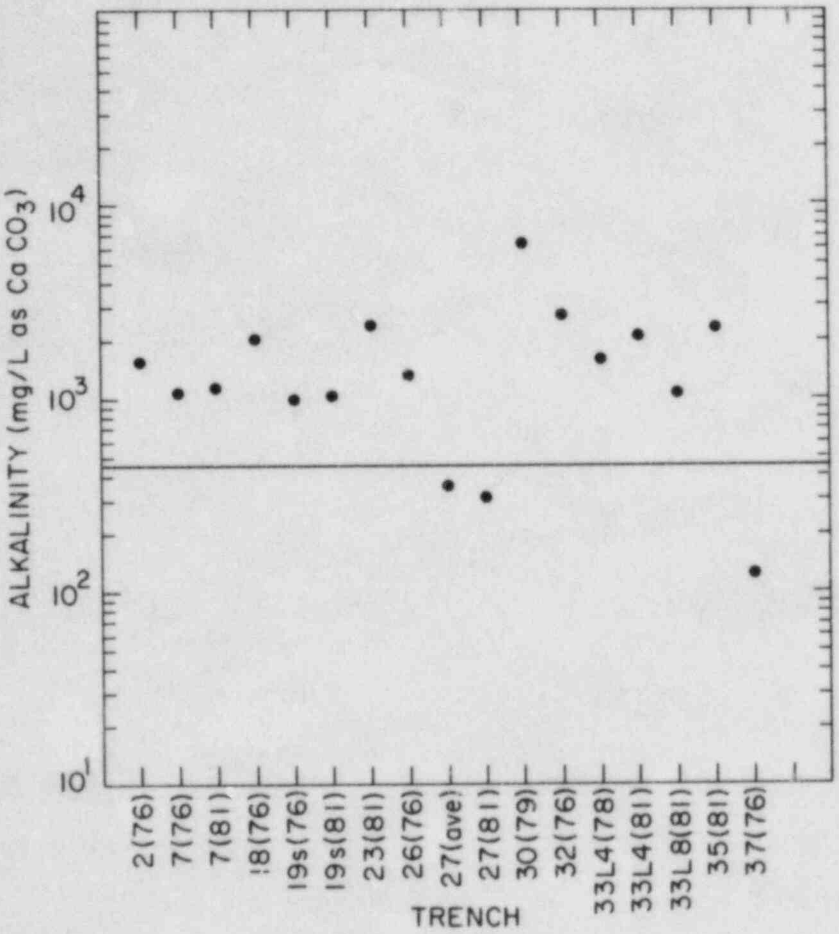


Figure 4.7. Alkalinity contents of trench leachates relative to ambient groundwater (solid line).

In terms of the principal inorganic leachate constituents known to be modified by microbial degradation of organic matter, Figure 4.8 shows that relative to ambient groundwater (well water UA3), most trench leachates exhibit significant sulphate depletion, and elevated levels of ammonia and titration alkalinity ($CO_3^{2-} + HCO_3^{-}$).

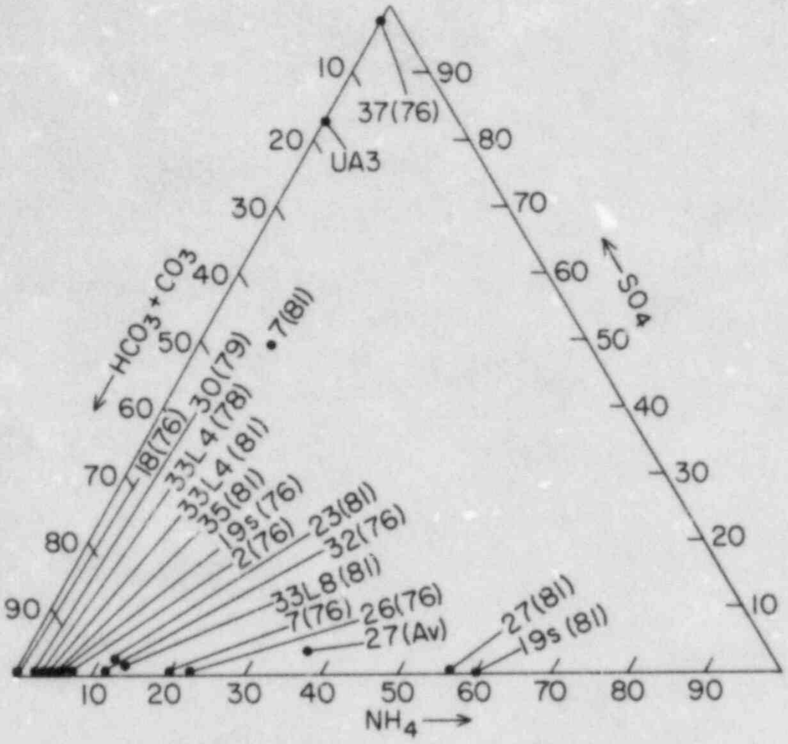


Figure 4.8 Ternary plot showing the nature and extent of modification of infiltrated rainwater as a result of microbial degradation processes. UA3 represents the composition of ambient groundwater.

4.1.1.3. Microbial Degradation of Organic Solutes

A microbiological study of the trench leachates, revealed that: (a) aerobic and anaerobic sulphate reducing, denitrifying, and methanogenic bacteria are present in the leachates; (b) mixed cultures isolated from the leachates are able to grow anaerobically in trench leachates; and (c) the organic compounds in the leachates are utilized by the bacteria as a carbon source for growth.

Microbial degradation of the organic constituents of the waste under anaerobic conditions can result in the production of gases such as CO_2, CH_4, H_2, and several organic acids and alcohols. Laboratory work at BNL demonstrated that methane bacteria present in the leachates produced appreciable amounts of tritiated and carbon-14 methane in the leachates. Several of the low molecular weight organic acids are formed in the trenches due to breakdown of complex organic materials and can be further metabolized by microorganisms. Among the hydrophilic organic compounds identified in the trench leachates, some of the monocarboxylic and dicarboxylic acids are believed to be common metabolic intermediates. Some of these acids could also be initially waste derived. The unoxygenated carboxylic acids could be a product of microbial degradation of unoxygenated carboxylic acids and/or alkanes

(Robertson, 1984). Recently, Kirby et al. (1984) reported that EDTA-like species, ethylenediaminetriacetic acid (ED3A), which was identified in the leachates and does not appear to be commercially available as a chelating agent, may be a biodegradation product of N-hydroxyethylenediaminetriacetic acid (HEDTA) or ethylenediaminetetraacetic acid (EDTA).

Although microbial degradation of organic solutes in anaerobic environments proceeds slowly, it is not clear which of the organic compounds found in the leachates are further degraded and to what extent. For this purpose, A. J. Francis (Weiss and Colombo, 1980) conducted laboratory experiments on trench leachates 26 and 32. A mixed culture bacteria isolated from each of the leachates was used to inoculate the respective filter-sterilized leachates in serum bottles filled with N_2. Uninoculated, filter-sterilized control samples were incubated under identical conditions. After 30 days of incubation at 28°C, the inoculated and the control samples were analyzed for the organic constituents by gas chromatography and mass spectrometry as described in detail elsewhere (Weiss and Colombo, 1980).

The observed changes in concentrations of several organic constituents due to microbial activity are shown in Tables 4.2 and 4.3. Changes in concentrations of several acidic organic compounds were observed in both the leachate samples. However, little degradation of tributyl phosphate and α-terpineol was observed. Several of the low molecular weight organic acids are formed due to breakdown of complex organic materials and are further metabolized by microorganisms; hence these compounds are in a dynamic state of being both synthesized and destroyed.

Table 4.2. Anaerobic degradation of organic compounds present in trench leachate 26 by a mixed culture bacteria.

Compound	Initial Concentration (mg/L)	Change in Concentration (%)
2-Methylpropionic acid	3.5	+ 31
2-Methylbutanoic acid	19	+ 16
Valeric acid	4.6	-100
C_6 acid (unidentified)[a]	N.Q.[b]	+ 6
C_6 acid (unidentified)[a]	N.Q.	+ 4
Hexanoic acid	1.8	-100
2-Methylhexanoic acid	1.3	+ 8
Cresol	1.8	+ 11
C_8 acid (unidentified)[a]	N.Q.	- 4
C_8 acid (unidentified)[a]	N.Q.	- 1
Benzoic acid	1.1	0
Phenylacetic acid	1.4	- 7
Phenylpropionic acid	1.2	-100
α-Terpineol	0.16	- 6

[a] Percent change in concentration was determined on the basis of the ratio of the compound with the internal standard.

[b] N.Q. = not quantified.

Table 4.3. Anaerobic degradation of organic compounds present in trench leachate 32 by a mixed culture bacteria.

Compound	Initial Concentration (mg/L)	Change in Concentration (%)
2-Methylpropionic acid	5.9	- 2
2-Methylbutyric acid	21	- 52
3-Methylbutyric acid	9.9	0
Valeric acid	5.5	+ 27
2-Methylpentanoic acid[a]	N.Q.[b]	- 24
C_6 acid (unidentified)[a]	N.Q.	- 27
Phenol	1.1	- 27
Hexanoic acid	5.1	- 45
2-Methylhexanoic acid	3.0	- 10
Cresol (isomers)	3.9	- 21
C_8 acid (unidentified)[a]	N.Q.	- 13
Benzoic acid	1.9	- 26
Octanoic acid	1.9	- 21
Phenylacetic acid	3.8	- 50
Phenylpropionic acid	9.3	- 53
Phenylhexanoic acid	N.Q.	- 11
α-Terpineol	0.26	- 12
Tributyl phosphate	0.24	0

[a] Percent change in concentration was determined on the basis of the ratio of the compound with the internal standard.

[b] N.Q. = not quantified.

The findings suggest that several of the low molecular weight organic acids can be formed due to breakdown of complex organic material. In addition, some of these compounds can be further metabolized by microorganisms, indicating that both the sources and sinks for certain organic compounds are time dependent and a function of the nature and intensity of microbial activity. Since some of these organic compounds are known to solubilize radionuclides by complex formation and enhance radionuclide mobility, it is important to know the dynamics of the system in terms of both synthesis and destruction of certain organic compounds in a given trench. This can have a significant effect on the solubilization, mobility and transport of several radionuclides.

4.1.2. Leaching of Buried Waste

Water accumulations in the trenches lead to prolonged leaching of buried waste materials, resulting in the presence and build up of various waste derived constituents in the leachates. The nature and extent of modification of infiltrated water due to waste leaching is a function of the quantity and characteristics of the waste and the residence time of accumulated water. The water accumulations in the trenches at Maxey Flats have a relatively long residence time, which allows continuous leaching of waste materials for extended time periods contributing to leachate formation. As a consequence, the resulting leachates exhibit enrichments, to varying degrees, of waste-derived inorganic, organic and radionuclide constituents associated with fuel and non-fuel cycle low-level wastes (Appendix A).

4.1.2.1. Enrichment of Waste-Derived Constituents

Inorganic Constituents

The important inorganic constituents that were found to be significantly enriched in most trench leachates relative to ambient groundwater are Na^+, K^+, Fe^{2+}, Mn, Cl^- and dissolved inorganic carbon. Table 4.4 shows the extent of enrichment of the various constituents relative to ambient groundwater in each trench leachate. For example, all trench leachates except 33L8 show significant enrichment in Cl^-, with leachates 7(81), 27(Av), and 27(81) concentrations being more than an order of magnitude greater than that of ambient groundwater (Figure 4.9). The chloride concentration in leachate 27 (Av) is elevated by a factor of ≈70.

Relative to ambient groundwater, several trench leachates are enriched in sodium by factors varying from 1.6 for leachate 27(Av) to a high of 8.7 for leachate 7(81). Leachates 7(76), 19s(81), 26(76), 33L4 (78,81), however, exhibit concentrations close to that of the groundwater (Figure 4.10). Both leachates 19s(76) and 33L8(81) are depleted in Na^+ by factors of 3 and 5, respectively.

Like Cl^-, potassium is enriched in all trench leachates, except 33L8(81) [Table 4.4, Figure 4.11]. The small depletion observed in leachate 37(76) is perhaps not significant. Like Na^+, the maximum enrichment (14x) of K^+ relative to groundwater is observed in leachate 7(81). It should be noted that chloride was also significantly enriched in leachate 7(81). Similar to the observed depletion of Na^+ and Cl^- in leachate 33L8(81), potassium exhibits a similar pattern.

As evident from the enrichment plots, both dissolved iron (Figure 4.12) and manganese (Figure 4.13) show enrichments of varying degrees in most trench leachates. The enrichment factors for dissolved iron vary from a low of two for leachate 33L4(81) to a high of 12,000 for leachate 27(Av). In contrast, leachate 27(81) is only enriched by a factor of 1,600. As discussed later, a major fraction of the total dissolved iron, believed to be a by-product of corrosion of steel drums commonly used for packaging wastes, is present as Fe^{2+} ion. This is also consistent with the anoxic redox conditions of most leachates. Leachates 23(81) and 33L4(81) show no significant enrichment or depletion of manganese, while 18(76) and 33L4(81) are depleted by factors of three and two, respectively. Like dissolved iron, dissolved manganese shows maximum enrichment in leachate 27(Av) [1,200x]. In comparison, leachate 27(81) is enriched by a factor of 17. Although the oxidation state of Mn was not determined, one would expect, based on existing redox conditions in the trenches, most of the dissolved manganese to be present as Mn^{2+}. Furthermore, based on Figure 4.2, complete reduction of manganese oxides to Mn^{2+} occurs before reduction of iron oxides can take place. Since most of the dissolved iron is present as Fe^{2+}, one can assume that manganese is present as Mn^{2+} as well.

Table 4.4. Enrichment of leachate constituents due to waste leaching.

	Enrichment Factors[a]						
Leachate	DOC[b,d]	DIC[b,d]	Na^+	K^+	Mn_T[c,d]	Fe_T[c,d]	Cl^-
	$(x10^{2})$	$(x10^{0})$	$(x10^{0})$	$(x10^{0})$	$(x10^{0})$	$(x10^{2})$	$(x10^{0})$
2(76)	0.3	6.1	2.3	2.8	7.5	4.0	4.4
7(76)	0.2	4.7	0.8	5.8	5.0	6.1	3.1
7(81)	1.2	4.9	7.1	14	19	1.6	36
18(76)	0.8	9.9	1.8	2.1	0.3	3.3	4.4
19s(76)	1.0	1.8	0.3	1.0	7.6	15	2.1
19s(81)	0.7	17.0	0.8	1.1	5.0	6.5	3.3
23(81)	1.3	11.7	2.8	3.4	1.0[e]	0.7	8.2
26(76)	1.5	3.4	0.8	1.6	7.4	6.5	4.1
27(Av)	1.0	0.6	1.6	3.5	1200	120	68
27(81)	0.8	1.3	1.8	3.6	17	16	33
30(79)	0.4	33.7	3.3	1.8	3.2	1.0	0.05
32(76)	1.3	11.5	2.3	8.8	12	1.6	5.3
33L4(78)	1.7	0.2	0.6	1.2	0.5[e]	0.03	2.4
33L4(81)	2.4	0.02	0.6	4.2	1.0[e]	0.02	5.2
33L8(81)	0.3	7.4	0.2	0.5	18	4.3	0.5
35(81)	0.9	8.8	2.0	2.1	3.0	0.09	3.4
37(76)	5.3	0.5	2.3	0.8	420	110	2.6

[a] Enrichment factor = C_t/C_w, where C_t represents concentration of leachate species and C_w, the well water species concentration as reported by Zehner (1983) for well UA3.

[b] DOC = dissolved organic carbon; DIC = dissolved inorganic carbon.

[c] Mn_T, Fe_T represent total dissolved manganese and iron, respectively.

[d] Since C_w was not available for these species in well water UA3, well water UB1A concentrations were used instead for calculating enrichment factors.

[e] Detection limits of species in leachate were used to calculate enrichment factors.

Like the other inorganic constituents discussed above, dissolved inorganic carbon also shows considerable enrichment in most trench leachates (Figure 4.14). Only leachate 33L4 shows depletion in dissolved inorganic carbon compared to ambient groundwater. Among the leachates studied, leachate 30(79) is observed to be the most enriched in dissolved inorganic carbon (100x).

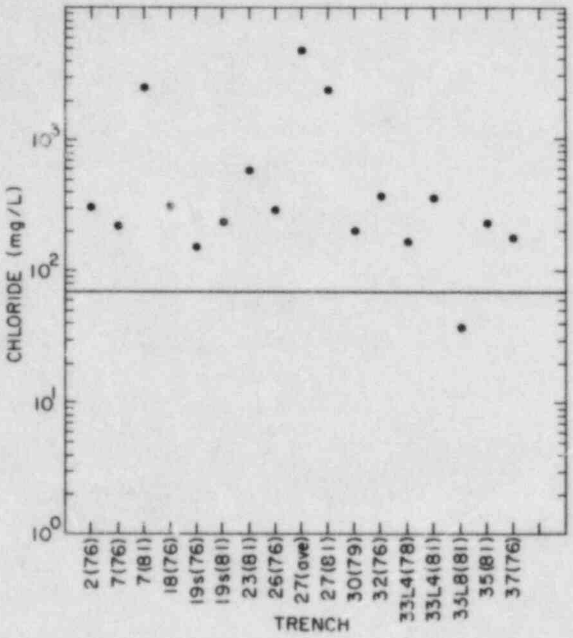


Figure 4.9. Chloride concentrations in trench leachates relative to ambient groundwater (solid line).

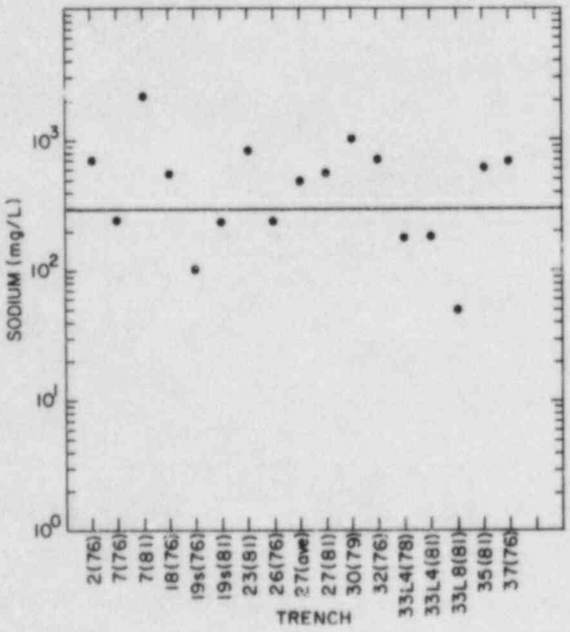


Figure 4.10. Sodium concentrations in trench leachates relative to ambient groundwater (solid line).

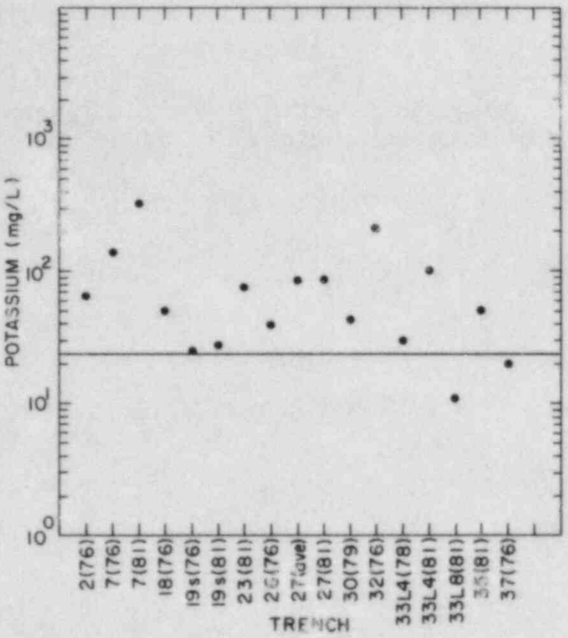


Figure 4.11. Potassium concentrations in trench leachates relative to ambient groundwater (solid line).

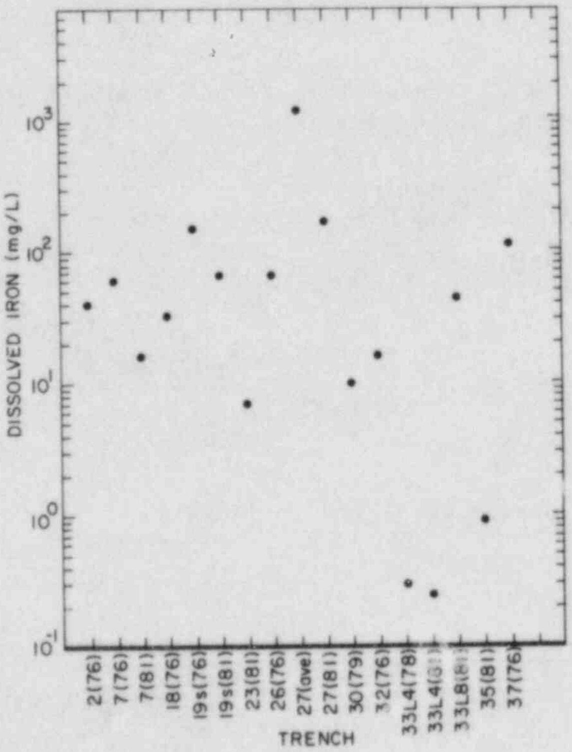


Figure 4.12. Dissolved iron concentrations in trench leachates relative to ambient groundwater (solid line corresponding to 0.1 ppm concentration).

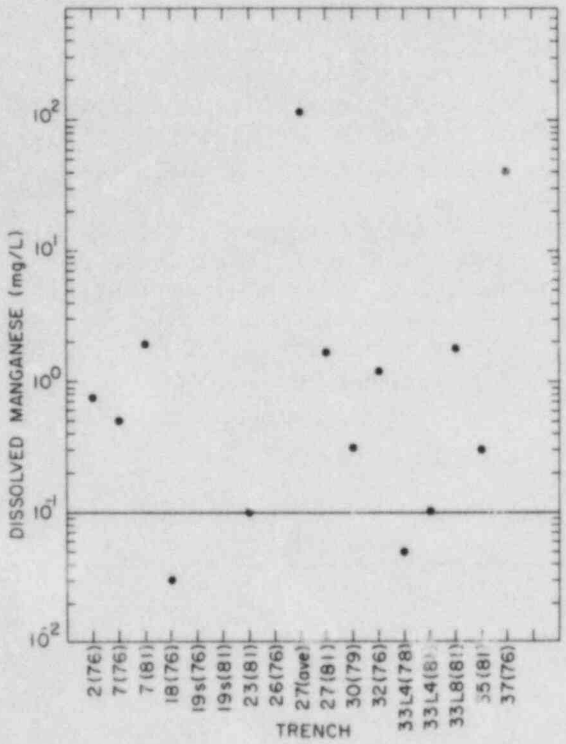


Figure 4.13. Manganese concentrations in trench leachates relative to ambient groundwater (solid line).

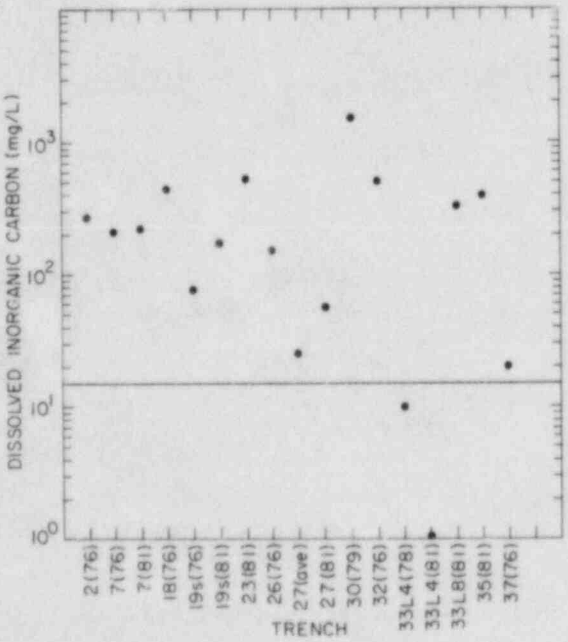


Figure 4.14. Dissolved inorganic carbon concentrations in trench leachates relative to ambient groundwater (solid line).

The enrichments of Na^+, K^+, Cl^-, and other inorganic constituents are also reflected in the high specific conductance of the leachates, especially for leachates 7(81) and 27(Av) [Figure 4.15]. Relatively low specific conductance is observed for leachate 33L8(81) which is also depleted in several inorganic constituents, relative to groundwater.

In addition to the principal waste-derived inorganic constituents discussed above, there are several other constituents which are present in elevated concentrations in many leachates sampled. Significant enrichments of the following constituents are observed: Ca^{2+} and high pH in leachate 33L4(78,81), Mg^{2+} in leachate 30(78), Ba^{2+} and Sr^{2+} in 27(Av), 27(81), and 33L4(78,81), Li^+ in 18(76) and 19s(76), F^- in 7(81) and 35(81), SO_4^{2-} in 7(81) and 37(76), NO_3- in 23(81) and 27(81), and SiO_2 in 30(79) and 37(76).

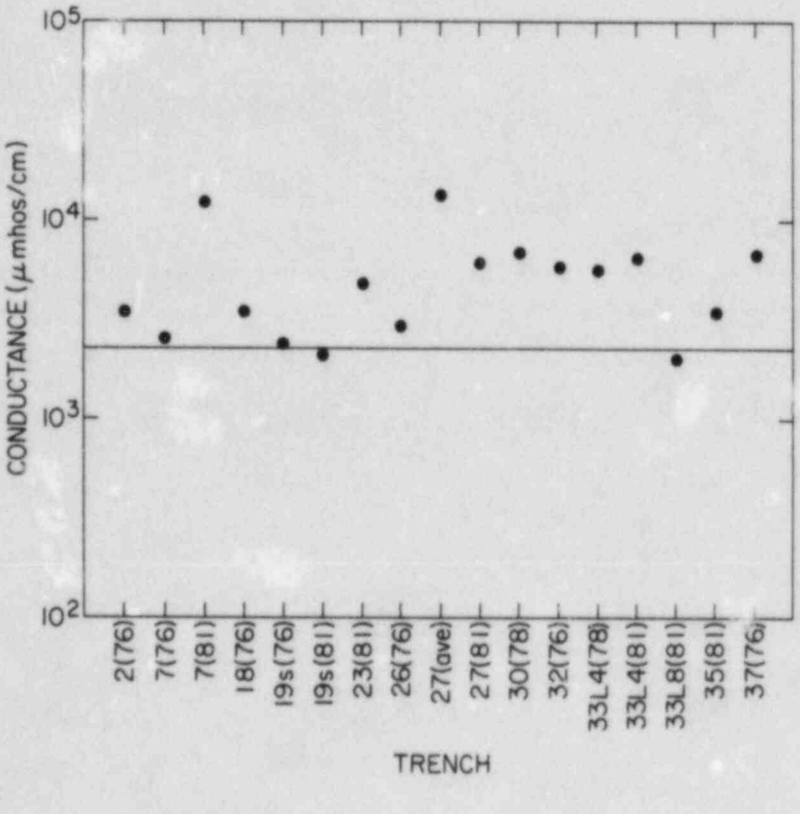


Figure 4.15. Specific conductance of trench leachates relative to ambient groundwater (solid line).

Dissolved Radionuclides

The 1977 survey radionuclide data and the decay corrected average radionuclide data based on multiple trench samplings during the period 1976-1981 show that substantial amounts of H-3, Co-60, Sr-90, Cs-137, and Pu isotopes (Pu-238; Pu-239,240) are found in most trench leachates. In many leachates, Cs-134 and Am-241 are also present. In addition, Na-22 and Mn-54 are observed in several leachate samples.

Tritium is the most abundant of the radionuclides identified and is invariably present in all trench leachates. Its presence and relatively high concentrations can be attributed to the readily leachable nature of H-3 present in waste materials. Chemically bound as HTO, tritium is the most mobile radionuclide among those identified in the trenches. Because tritium does not participate in precipitation reactions and is not removed by sediment, it behaves conservatively and could serve as an inert tracer for evaluating the nature and extent of waste leaching.

The types of radionuclides and their concentration levels observed in the leachates reflect to a large extent the nature and extent of leaching as determined by the reactivity and quantity of waste materials, the leach behavior of the radionuclides, the redox and chemical environment of the trenches. For example, most leachates sampled from "L" series trenches invariably exhibit concentrations of Cs-137, Cs-134, Co-60, and Am-241 below their detection limits. This could very well be a result of solidification of liquid wastes disposed of in these trenches. In the case of trench 33L18, the liquid wastes were solidified with ureaformaldehyde (UF). Earlier work at Brookhaven National Laboratory has shown that leaching of UF generates a considerable amount of acidity. The pH of the leachates was observed to be around 2.0 pH units. As a result of strongly acidic conditions in trenches 33L3 and 33L18 (Weiss and Colombo, 1980), leaching of waste materials is more intense thus giving rise to high concentrations of waste-derived radionuclide constituents. The high concentrations of dissolved organic constituents, especially the complexing agents, also tend to keep the radionuclides, such as the Pu isotopes and Co-60, in solution and thus raise their concentrations as well as make them more mobile.

Organic Constituents

As shown in Figure 4.16, the concentrations of total dissolved organic carbon in trench leachates are significantly elevated relative to ambient groundwater. The degree of enrichment varies by a factor of 20 for leachate 2(76) to a high of 530 for leachate 37(76). Several leachates are enriched in dissolved organic carbon by more than two orders of magnitude, compared to local groundwater composition (Table 4.4).

Tables 4.5 and 4.6 show the various hydrophobic and hydrophilic organic compounds identified in the trench leachates. The hydrophobic organic compounds present consist of straight- and branched-chain aliphatic acids, aromatic acids, alcohols, aldehydes, ketones, amines, aromatic hydrocarbons, ester, ethers, and phenols. Among the hydrophilic organic compounds, the classes of compounds consisted of chelating agents, carboxylic acids, oxygenated acids, and phthalates.

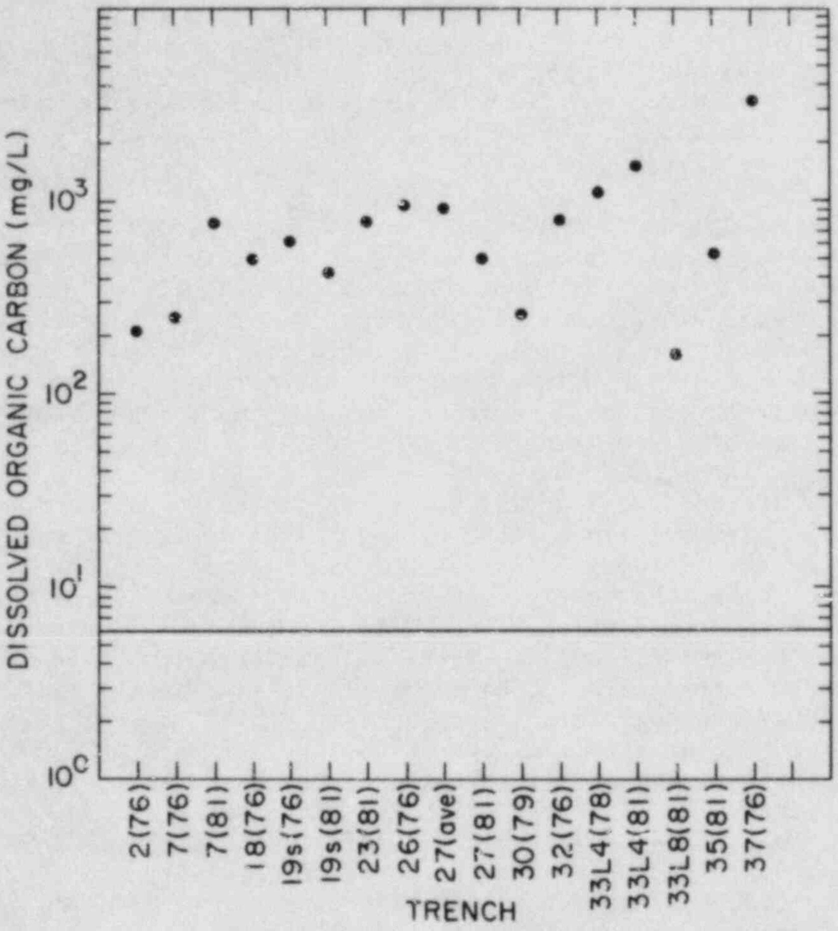


Figure 4.16. Total dissolved organic carbon in trench leachates relative to ambient groundwater (solid line).

The types of most compounds identified reflect to a large extent the nature of the buried organic waste materials. Solvents or scintillation fluids, such as p-dioxane, toluene, and xylene are present. Tributyl phosphate is presumably derived from the process of solvent extraction of metal ions from solution of reactor products. Chelating agents such as EDTA, NTA, and DTPA are commonly used as chemical decontamination agents in power plants. Some of these compounds such as tributyl phosphate, methyl isobutyl ketone, phthalates, aniline, cyclohexylamine, and chelating agents have the potential to form radionuclide complexes and thus enhance radionuclide mobility.

Many of the water soluble organic compounds identified in the trench leachates, especially the straight and branched chain organic acids, could be metabolic products formed as a result of anaerobic degradation of organic wastes.

Table 4.5. Waste-derived hydrophobic organic compounds in trench leachates[a]

Compound Class	Specific Compounds
Carboxylic acids	Benzene acetic acid
	Benzene propanoic acid
	Benzoic acid
	C5 acids
	C6 acids
	C8 acids
	2.5-Dimethylbenzene butanoic acid
	2-Ethylhexanoic acid
	Hexanoic acid
	Isobutyric acid
	Methylbenzoic acid
	2-Methylbutanoic acid
	3-Methylbutanoic 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
	Phthalic acid
	Phthalic anhydride
	Toluic acid
	Valeric acid
Esters	Dibutylphthalate
	Diethylphthalate
	Dioctyl adipate
	Di-Isooctyl phthalate
	Methyl methacrylate
	Methyl ethyl tripropylene glycol
	Phthalate ester
	Triethyl phosphate
	Tributyl phosphate
Sulfonamides	N-Butylbenzene sulfonamide
	N-Methylbenzene sulfonamide
	C2-Toluene sulfonamide
	C3-Toluene sulfonamide

Table 4.5. Waste-derived hydrophobic organic compounds in trench leachates[a] (continued).

Hydrocarbons	Alkanes (C20–C31) Dimethyl naphthalene Dodecane Naphthalane Toluene Xylene (isomers) Tridecane Undecane
Hydrocarbon halides	Bromodichloromethane Chloroethlybutene Dichloroiodomethane Dichloromethylbutane
Alcohols	Cyclohexanol Diethylene glycol Ethylene glycol 2-Phenylcyclohexanol Polyethylene glycol Polyethylene glycol oligomers 2-Ethyl-1-Hexanol α-Terpineol
Phenols	Cresol isomers Phenol 4-T-Butylphenol Vanillin Vanillone
Ketones and Aldehydes	2-Butanone Camphor Cyclohexanone Dibutylketone Fenchone 4-Hydroxybenzaldehyde Methylbutenone Methylisobutyl ketone
Amines	Aniline N,N-Bis (Phenlymethyl) amine Dicyclohexyl amine Cyclohexyl amine Pyridine

Table 4.5. Waste-derived hydrophobic organic compounds in trench leachates[a] (continued).

Esters	Alkylphenoxy oligomers BIS (2-Chloroethyoxy) ethane BIS (2-Chloroethyoxy) methane BIS (2-Chloroethyl) ether BIS (2-Chloromethyl) ether Tripropyleneglycol methyl ethyl BIS (1-Methoxyethyl) ether BIS (2-Ethoxyethyl) ether Diethylene glycol diethyl ether
Heterocyclics	Barbital Benzofuran Benzothiazol 2 (3H)-Benzothiazolone Caffeine Caprolactam 1,3-Dihydro-2H-Indol-2-One P-Dioxane Nicotine Pentabarbital Piperidinone Tetrahydrofuran

[a] Based on leachate samplings and analyses conducted by both BNL and PNL.

Table 4.6. Waste-derived hydrophilic organic compounds in trench leachates[a]

Compound Class	Specific Compounds
Chelating agents	Diethylenetriaminepentaacetate (DTPA) Nitrilotriacetic acid (NTA) Ethylenediaminetetraacetic acid (EDTA) N-Hydroxyethylethylenediaminetriacetic acid (HEDTA) Ethylenediaminetriacetic acid (ED3A)[b]
Dicarboxylic acids	Oxalic acid Succinic acid Methylsuccinic acid Pentanedioic acid Hexanedioic acid Methylhexanedioic acid Octanedioic acid Nonanedioic acid
Monocarboxylic acids	Dodecanoic acid Hexadecanoic acid Nonanoic acid Hexadecanoic acid Octadecanoic acid
Oxygenated acids	Citric acid 4-Oxo-Pentanoic acid Benzoic acid 2-Hydroxybenzoic acid 1,3-Benzenedicarboxylic acid 1,4-Benzenedicarboxylic acid 1,2,4-Benzenetricarboxylic acid
Phthalates	Dibutyl phthalate Dimethyl phthalate Methylpropyl phthalate Dioctyl phthalate

[a] Based on leachate samplings conducted by BNL and analyses by PNL.

[b] Kirby et al. (1984) reported that ED3A may be a degradation product of HEDTA or EDTA.

4.1.2.2. Effect on Solute Chemistry

The ternary plot in Figure 4.17 summarizes the nature and extent of modification of infiltrated water as a result of leaching of buried waste materials. The end components in the ternary plot represent the principal suites of inorganic constituents which are believed to be waste-derived, based on discussion in the previous section of this report. Relative to the composition of groundwater represented by well water UA3, the compositions of most trench leachates reflect enrichment in the constituents (Na + K + Cl + F + NO_3) and depletion of (Ca + Ba + Sr) and Mg. Only leachates 33L4(78,81) and 33L8(81) are enriched in (Ca + Sr + Ba), depleted in Mg and (Na +K + Cl + F + NO_3), reflecting leaching of the cementitious matrix, which was used as a binder for solidification of the liquid wastes in these trenches. In contrast, 30(79) and 37(76) are the only leachates which exhibit substantial enrichment of Mg and depletion of other waste-derived components with the overall composition approaching that of ambient groundwater. Therefore, in terms of waste-derived inorganic constituents, leachates 30(79) and 37(76) appear to be the least modified relative to ambient groundwater. The maximum modification in the composition of infiltrated rainwater as a result of waste leaching is reflected in the compositions of trench leachates 33L4(78,81) and 7(81).

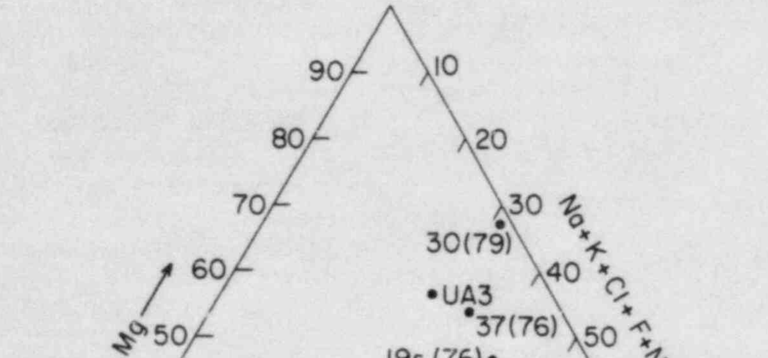


Figure 4.17. Ternary plot showing the nature and extent of modification of infiltrated rainwater as a result of leaching of buried waste materials. UA3 represents the composition of ambient groundwater.

4.1.3. Saturation States and Precipitation Reactions

In addition to waste leaching and microbial degradation reaction controls on trench leachate compositions, the leachate solutes are also subject to abiogenic precipitation reactions, especially in relatively stagnant systems such as those at Maxey Flats where the products of waste leaching and mircobial dedegradation are continually generated and subsequently accumulate. To evaluate equilibrium controls on leachate chemistry, WATEQF geochemical code (Plummer, Jones, and Truesdall, 1983) was used to calculate saturation states of trench leachate solutes with respect to given mineral phases.

In the solubility calculations, total titration alkalinity was assumed to be equal to carbonate alkalinity. Only carbonate, sulphate, phosphate, fluoride, and sulphide mineral formations have been considered. Ideally, such solubility calculations should be done in conjunction with direct analysis of particulate matter in leachate or sediment for detailed chemical or mineralogical composition, especially for the sulphide and carbonate phases. However, in the present study, the main emphasis was placed on solute chemistry. No attempt was made to characterize the solid phases.

In Table 4.7 we have presented the mineral solubility products and the reactions used in the WATEQF program code to calculate saturation states. Figure 4.18 and Table 4.8 show the calculated saturation indices (log IAP/KT) for the carbonate, sulphate, phosphate, fluoride, and sulphide minerals plotted for each trench leachate sample. The horizontal bars on either side of the equilibrium line (log IAP/KT = 0) represent 5% tolerance limits on saturation index values due to uncertainties in the values of mineral solubility products.

Table 4.7. Solubility products at 25°C and 1 atm for selected mineral phases.

Reaction		Solubility Product[a] (log Ksp)
$CaCO_3$ (Calcite)	$\rightleftarrows Ca^{2+} + CO_3^{2-}$	-8.5
$CaMg(CO_3)_2$ (Dolomite)	$\rightleftarrows Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$	-16.9
$FeCO_3$ (Siderite)	$\rightleftarrows Fe^{2+} + CO_3^{2-}$	-10.5
$MnCO_3$ (Rhodochrosite)	$\rightleftarrows Mn^{2+} + CO_3^{2-}$	-10.5
$CaSO_4 \cdot 2H_2O$ (Gypsum)	$\rightleftarrows Ca^{2+} + SO_4^{2-}$	-4.8
$BaSO_4$ (Barite)	$\rightleftarrows Ba^{2+} + SO_4^{2-}$	-10.1
CaF_2 (Fluorite)	$\rightleftarrows Ca^{2+} + 2F^-$	-12.3
$Fe_3(PO_4)_2 \cdot H_2O$ (Vivianite)	$\rightleftarrows 3Fe^{2+} + 2PO_4^{3-}$	-36.0
FeS_2 (Pyrite)	$\rightleftarrows Fe^{2+} + 2S^{2-}$	-18.6
FeS (Amorphous)	$\rightleftarrows Fe^{2+} + S^{2-}$	-16.9[b]
FeS (Mackinawite)	$\rightleftarrows Fe^{2+} + S^{2-}$	-17.5[b]

[a] The K_{sp} values are reported by Plummer et al. (1983).

[b] The K_{sp} values for amorphous FeS and mackinawite are those reported by Aller (1983).

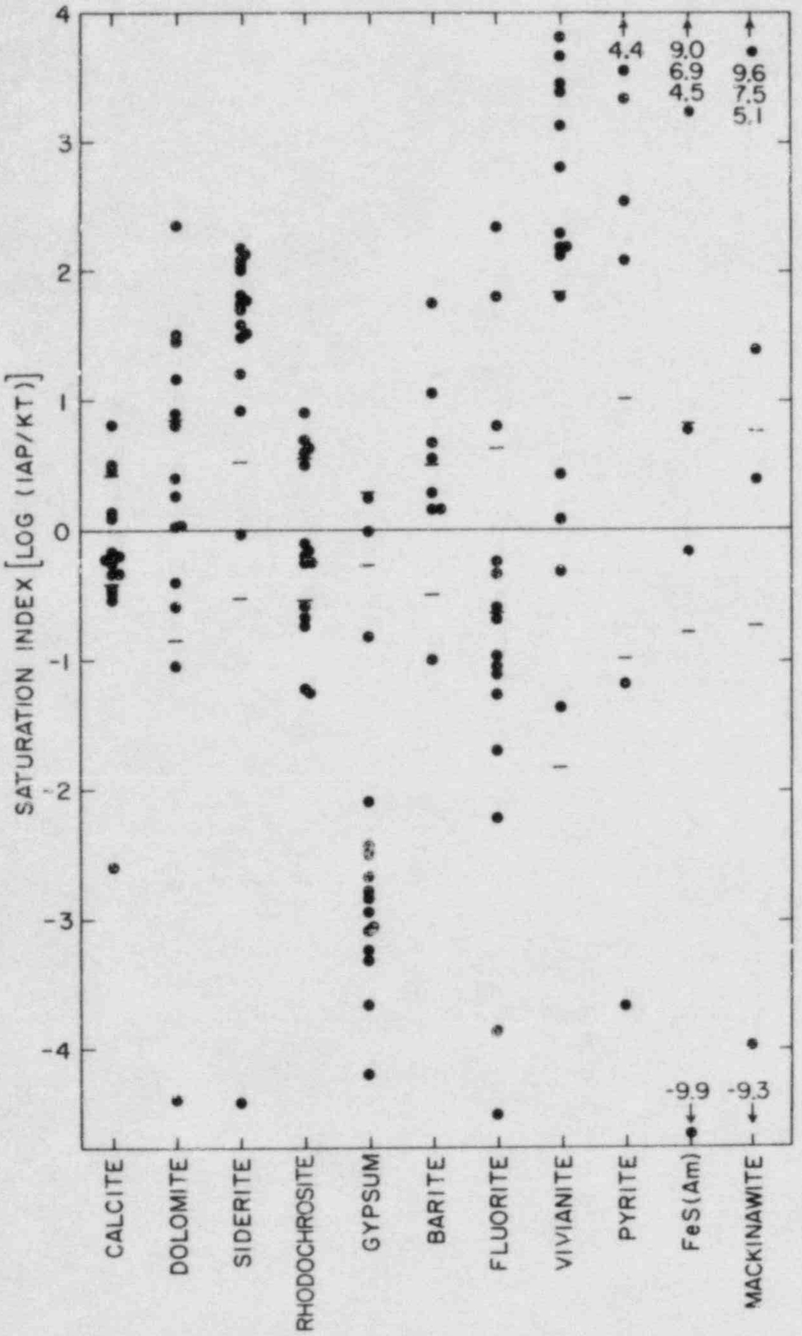


Figure 4.18. Calculated ion activity products for the major solutes in trench leachates compared to solubility products of selected minerals expected to form under anoxic conditions. The comparisons are made in terms of saturation index [Log (IAP/KT)]. Closed circles represent calculated saturation indices based on observed leachate compositions for the various minerals. Horizontal bars represent 5% tolerance limits on saturation indices due to uncertainties in the values of mineral solubility products (K_{sp}).

Table 4.8. Ratios of ion activity products to mineral solublity constants (log IAP/KT) for Maxey Flats trench leachates.[a,b]

Trench	Calcite	Dolomite	Siderite	Rhodochrosite	Gypsum	Barite	Fluorite	Vivianite	Pyrite	FeS (Am)	Mackinawite
2(76)	-0.33	0.004	1.74	-0.19	-3.05		-1.27	2.29			
7(76)	0.44	0.89	2.06	-0.21	-2.46		-0.62	3.39			
7(81)	0.51	1.49	1.57	0.59	-0.83	1.75	2.33	2.18	-10.9	0.80	1.40
18(76)	-0.25	0.81	2.08	-1.22	-3.27		-1.71	2.80			
19a(76)	-0.17	0.27	2.17	-0.27	-2.81		-0.98	3.66			
19a(81)	-0.50	-0.42	1.49	-0.74	-3.62	-0.67	0.25	2.14	0.97	6.87	7.47
23(81)	0.09	1.69	1.81	-0.27	-2.97	0.56	-0.39	1.81	-12.5	-10.2	0.41
26(76)	-0.23	0.41	2.03	-0.11	-3.08		-3.87	3.13			
27(79)	0.75	-1.26	1.40	0.48	-3.00	0.15	-0.42	2.10	9.92	9.04	9.64
27(81)	-0.21	-0.005	1.51	0.49	-3.34	0.29	-0.69	3.44	-5.01	3.26	3.86
30(79)	-0.24	1.29	1.20	-0.67	-2.68	1.04	-4.46	-0.57	-25.7	-9.90	-9.30
32(76)	0.82	2.34	2.10	0.69	-2.86		-1.05	2.43			
33L8(81)	-0.34	-1.05	0.92	-0.59	-2.08	0.16	0.79	0.09	-25.7	-4.67	-4.07
35(81)	1.11	3.52	1.59	0.89	-4.18	-1.01	1.79	0.43	-1.38	4.51	5.11
37(76)	-2.59	-4.39	-0.02	-1.24	-0.01		-1.03	-1.38			

[a] Calculations based on geochemical code WATEQF (Plummer et al., 1983).
[b] No entry indicates data not available.

The calculations show that most leachates tend to show saturation with calcite, dolomite, and rhodochrosite, implying that the Ca^{2+}, Mg^{2+}, Mn^{2+}, and CO_3^{2-} concentrations appear to be controlled by the precipitation of these mineral phases. Leachate 37(76), however, shows distinct undersaturation with respect to the three carbonate phases. This is consistent with the observation that the lowest alkalinity observed among all the leachates was for leachate 37(76). The saturation with respect to the carbonate phases is caused by the high carbonate concentrations resulting from the generation of CO_2 during microbial degradation of organic matter. High Mn^{2+} concentrations are presumably a result of the reduction of manganese oxide phases during anaerobic degradation process (Aller, 1983; Dayal et al., 1983).

As expected, most leachates exhibit undersaturation with respect to gypsum. This is not surprising, considering that sulphate concentrations are low due to the bacterial sulphate reduction process. In leachate 37(76), however, the SO_4^{2-} concentration appears to be controlled by gypsum solubility. It should be recalled that this is the only leachate sample that contains considerably high concentrations of sulphate (8000 mg/L). In the case of iron equilibria, all leachates are generally distinctly supersaturated with respect to siderite, pyrite, and iron monosulphides (amorphous FeS and mackinawite). Calculated supersaturations can be attributed to several factors: (a) Fe^{2+} is complexed by dissolved organic constituents; (b) the solubility products are incorrect; (c) other phases than carbonate formation are controlling Fe^{2+} concentrations. Consideration of other iron phases indicates that in leachates 23(81), 30(79), 33L8(81), 35(81), and 37(76) Fe^{2+} concentrations may be controlled by vivianite, a ferrous phosphate. However, other leachates show gross supersaturation with respect to the phosphate phase. It is quite conceivable that Fe^{2+} is complexed with chelating agents such as EDTA which has been reported to be present in most trench leachates. The net effect of iron complexation would be to suppress the Fe^{2+} activity and to increase its solubility.

In summary, solubility calculations based on trench leachate compositions indicate that calcite, dolomite, and rhodochrosite mineral phases are likely to form in the trench environments and exert control on the concentrations of Ca^{2+}, Mg^{2+}, Mn^{2+}, and CO_3^{2-}. In case of iron equilibria, gross supersaturations are found with respect to siderite, mackinawite, amorphous FeS, and pyrite. Some leachates exhibit saturation with respect to vivianite.

4.2. Waste Migration From Trenches

4.2.1. Oxidation Behavior of Anoxic Trench Leachates

Oxidation experiments were performed on several trench leachates to obtain some information on the behavior of anoxic trench leachates as they encounter a relatively less reducing environment along the groundwater flow paths. This information is important considering that the sorption characteristics and solubilities of several radionuclides, especially the actinides, are significantly different in oxidizing and reducing conditions. Furthermore, the development of a geochemical discontinuity, represented by ferric oxyhydroxide precipitation, following oxidation of iron-rich anoxic leachates, can have a profound effect on the migration of radionuclides.

Briefly, the oxidation experiments conducted at BNL involved the following laboratory procedures: an aliquot of each sample was anaerobically transferred into an oxidation chamber in an argon filled glove box and spiked with Sr-85, Cs-137, and Co-60. The pH, Eh, and alkalinity were determined immediately upon transfer by standard analytical methods (Franson, 1981). Further, an aliquot of the initial sample was acidified with HCl and analyzed for initial concentrations of ferrous iron, total iron, Cs-137, Sr-85, and Co-60. The oxidation chamber was removed from the glove box and the spiked trench water was exposed to air for approximately two weeks. Following complete air oxidation, the pH, Eh, and alkalinity were determined. The sample was filtered, acidified, and analyzed for Cs-137, Co-60, Sr-85, ferrous iron, and total iron. Details of the procedures used to analyze dissolved metals and gamma emitting radionuclides in the oxidation experiments are given elsewhere (Dayal et al., 1984).

The changes observed in pH, Eh, alkalinity, and radionuclide concentrations, upon air oxidation of radionuclide-spiked trench leachates, are presented in Table 4.9. The changes in the concentrations of Fe^{2+} and total dissolved iron are given in Table 4.10. Also listed in Table 4.10 are the acid generating potentials of the leachates, based on the ferrous to ferric oxidation reaction.

The results in Table 4.10 indicate that all trench waters, following oxidation, exhibit removal of most of the iron from solution, as a result of ferric oxyhydroxide precipitation. A reddish-brown precipitate was observed for all leachates, except leachate 33L4. As shown in Table 4.10, the initial dissolved iron concentrations in leachates 33L4 (78,81) are extremely low for a ferric oxyhydroxide precipitate to be observed following oxidation.

4.2.1.1. Ferric Oxyhydroxide Precipitation and Leachate Acidity

For the majority of trench waters, oxidation resulted in an increase in pH. A slight decrease in pH was observed for the trench leachate 33L4. This leachate is atypical of most Maxey Flats trenches, however, in that the disposed waste was in liquid form and subsequently solidified in a cement matrix. Another notable exception, leachate 27 having a high Fe^{2+} concentration and a low alkalinity, was discussed in a previous report (Pietrzak et al., 1983). Air oxidation of this leachate sample resulted in a drastic drop in pH. The pH changes can be attributed to a combination of three processes occurring simultaneously during oxidation: (a) loss of CO_2 as a result of exposure of the leachate to the lower partial pressure of CO_2 in air; (b) generation of acidity during oxidation of ferrous to ferric iron; and (c) neutralization of resulting acidity by trench water alkalinity. As discussed earlier, during the development of an anoxic water regime, bacterial degradation processes liberate carbon dioxide which raises the P_{CO_2} of the anoxic water. Upon exposure to air, the pH of naturally occurring anoxic waters normally rises, as a result of CO_2 loss and subsequent readjustment of the chemical system (Czyscinski and Weiss, 1981).

Table 4.9. Observed changes in pH, Eh, alkalinity, and radionuclide concentrations upon air oxidation of trench leachates.

Leachate	pH[a]		Eh (mV)[a]		Alkalinity (meq/L)[a]		Radionuclide in Solution After Oxidation (%)		
	Initial	Oxidized	Initial	Oxidized	Initial	Oxidized	Sr-85	Cs-137	Co-60
7(81)	7.5	8.1	-43	+402	25	19	86	104	97
19s(78)	6.9	8.5	+25	+397	18	17	b	b	b
19s(79)	7.1	8.2	-58	+399	21	18	86	101	98
19s(81)	6.7	7.7	-26	+411	22	19	92	100	92
23(81)	7.7	8.7	-95	+394	51	47	97	104	93
26(79)	6.5	8.3	-52	+413	19	19	92	94	90
27(78)	6.6	3.0	+17	+557	7	b	b	b	b
27(79)	6.6	3.0	+140	+300	6	b	b	b	b
27(81)	6.8	4.8	-43	+421	6	<0.5	99	100	95
30(79)	7.9	8.4	-37	+398	135	99	99	98	99
32(79)	7.9	9.0	-56	358	340	42	b	b	b
33L4(78)	12.1	11.6	-7	194	32	21	b	b	b
33L4(81)	11.3	10.8	+150	+246	34	23	88	104	99
33L8(81)	6.2	8.2	+79	+379	47	47	33	101	37
35(81)	8.2	8.4	-83	+399	47	47	94	101	92

[a] The initial measurements were made in the glove box immediately following sample transfer.
[b] Not determined.

Table 4.10. Changes in ferrous iron and total dissolved iron concentrations upon air oxidation of trench leachates.

Leachate	Dissolved Iron Concentration (mg/L)				Acid Generating[a] Potential [H^+] (meq/L)
	Initial		Oxidized		
	Fe^{2+}	Fe_T	Fe^{2+}	Fe_T	
7(81)	15	15	<1	0.4	0.54
19s(78)	b	115	b	b	4.1[d]
19s(79)[c]	53	49	<4	0.8	1.9
19s(81)[c]	68	71	<4	8	2.4
23(81)[c]	6	3	<1	0.3	0.20
26(79)	90	100	<4	1.1	3.2
27(78)	b	1150	b	b	41[d]
27(79)	1360	1400	b	b	49
27(81)	92	151	2	2	3.3
30(79)[c]	3	1.5	2	0.8	0.10
32(79)	b	0.4	b	b	0.01[d]
33L4(78)	b	0.3	b	b	0.01[d]
33L4(81)	<1	1.1	<1	0.2	<0.04
33L8(81)	23	45	<1	0.5	0.82
35(81)	2	1.5	<1	0.2	0.08

[a] Acid generating potential calculated based on oxidation of dissolved ferrous iron according to Eqs. (4.1) and (4.2).
[b] Not determined.
[c] The differences in the ferrous iron and total iron concentration are not significant, considering the analytical precision of the two methods.
[d] Assuming Fe_T exist as Fe^{+2} in solution.

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

$$Fe^{2+} + 1/4\ O_2 + H^+ \rightleftarrows Fe^{3+} + 1/2\ H_2O \qquad (4.1)$$

$$Fe^{3+} + 3H_2O \rightleftarrows Fe(OH)_3 + 3H^+ \qquad (4.2)$$

Each equivalent of ferrous iron that is oxidized and precipitated as ferric hydroxide produces two equivalents of hydrogen ion. Since all the dissolved iron is in the ferrous state in most trench leachates being studied and is available for oxidation, calculations show the acid generating potential in meq/L of H^+ which could be generated from the Fe^{2+} oxidation reaction (Table 4.10). However, the resulting acidity can be neutralized by the trench water alkalinity. The meq/L of the buffering capacity of each trench leachate available from the titration alkalinity is given in Table 4.9. The alkalinity data indicate that all leachates are relatively well-buffered, except leachate 27 which has a low alkalinity.

The changes in pH of trench water resulting from oxidation are interpreted in terms of these competing reactions. For leachates with high ferrous iron and alkalinity such as leachates 19s(78,79,81) and 26(79), the available buffering capacity is well in excess of that required to neutralize the acidity created during iron oxidation. The exception is leachate 27, where the acidity generated as a result of the oxidation of high concentrations of ferrous iron in solution is well in excess of the buffering capacity. Consequently, as discussed in an earlier report (Pietrzak et al., 1983), a sharp drop in pH is observed upon oxidation of leachate 27 which, in turn, inhibits complete oxidation of ferrous iron to ferric hydroxide. For leachates containing relatively low concentrations of Fe^{2+} iron such as trenches 23(81), 7(81), 30(79), 32(79) and 35(81) but with high alkalinity, exposure to air results in a release of excess P_{CO_2}, developed during bacterial degradation, and a subsequent rise in pH. Similar behavior has been reported in naturally occurring anoxic waters.

4.2.1.2. Balance Between Acidity and Alkalinity

The balance between acidity and alkalinity can be visualized in terms of a simple model as shown in Figure 4.19. Infiltrated rainwater interacts with buried waste materials and acquires a certain alkalinity, primarily from the CO_2 generated during microbial degradation of organic wastes. The amount of alkalinity acquired is a function of the characteristics, quantity, and reactivity of organic materials and the residence time of infiltrated water. Concurrently there is a build up of sulphide, as a result of sulphate reduction, and Fe^{2+}, derived from the leaching of waste materials and/or from corrosion of steel containers. As the anoxic leachate migrates along groundwater flow paths, oxidation of Fe^{2+} occurs, generating acidity which is neutralized by the alkalinity of the leachate. For the oxidation reaction to occur, it is assumed that there is sufficient O_2 present in the groundwater. If the anoxic leachate has a low buffering capacity and high Fe^{2+} concentration such as in leachate 27, where the acidity generated following oxidation is much greater than the initial alkalinity of the leachate, all the alkalinity will be consumed and an acid leachate will result. However, most Maxey Flats leachates are relatively well-buffered and, as a result, the acidity generated from oxidation of Fe^{2+} is not appreciable to neutralize the initial alkalinity and thus give rise to acid leachates along groundwater flow paths.

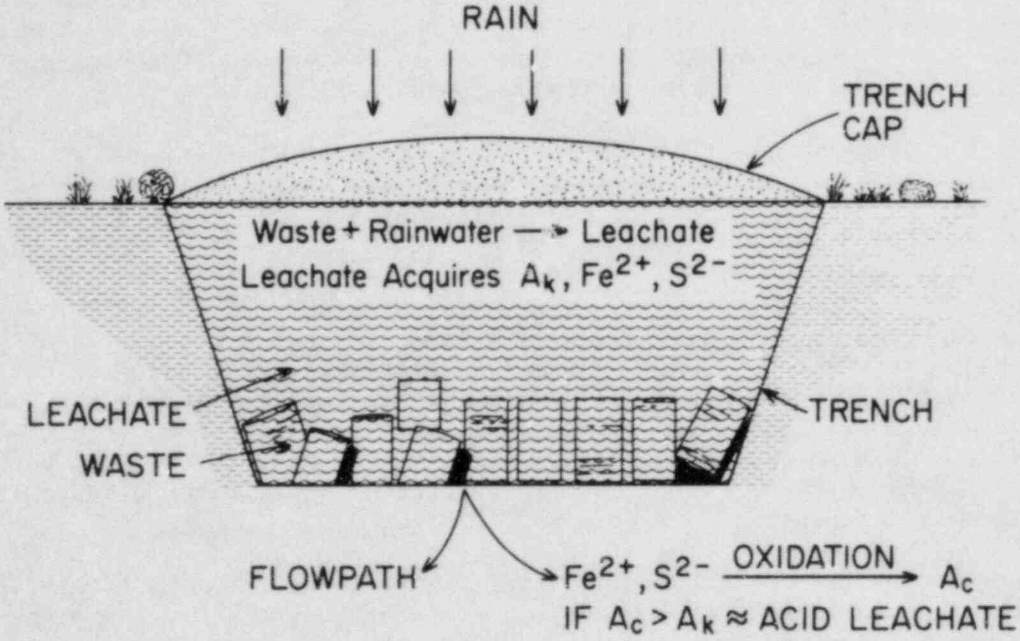


Figure 4.19. Generation of acid leachate visualized in terms of the balance between acidity (A_c) and alkalinity (A_k).

4.2.1.3. Leachate Oxidation and Saturation States

Although we have some idea of the mineral phases controlling the anoxic leachate chemistry, it is important to determine what mineral phases control the principal solute chemistry of the oxidized leachates, considering the fact that significant changes were observed in redox potential, pH, dissolved iron concentration, and alkalinity. All these changes reflect geochemical discontinuities in natural systems where iron-rich anoxic waters encounter an oxidizing environment.

Using the principal solute species of the anoxic and oxidized leachates, the ratios of ion activity products to mineral solubility constants (log IAP/KT) were calculated for calcite, dolomite, siderite, vivianite, and amorphous ferric hydroxide (Table 4.11). Figure 4.20 shows a plot of calculated saturation indices versus the principal mineral phases for the various anoxic and oxidized leachate samples.

Figure 4.20 indicates that, with respect to calcite and dolomite, most anoxic and oxidized leachates exhibit saturation to supersaturation. However, leachates 27(78, 79, 81), upon oxidation, show gross undersaturation relative to both calcite and dolomite. Only in leachate 27 was significant acidity generated following oxidation due to the initially low buffering capacity and high iron concentration. Assuming the Ca^{2+} and Mg^{2+} leachate concentrations to be the same before and after oxidation, the plot in Figure 4.20 indicates that leachate 27 upon oxidation is grossly undersaturated with respect to both calcite and dolomite in terms of its CO_3^{2-} content.

With respect to the iron equilibria in terms of siderite and vivianite, the anoxic leachates exhibit saturation to supersaturation with both iron mineral phases. Upon oxidation, however, all leachates are grossly undersaturated with respect to siderite and vivianite because most of the dissolved iron is transformed to Fe^{3+}.

As expected, practically all anoxic leachates are initially undersaturated with respect to amorphous ferric hydroxide. Following oxidation, however, all leachates, except 27, exhibit saturation to supersaturation. This is also confirmed by the observation that a reddish-brown ferric hydroxide precipitate formed upon air oxidation of most leachates. In the case of leachate 27, however, the high acidity present in the oxidized leachate tends to inhibit precipitation of $Fe(OH)_3$.

The solubility calculations indicate that, in addition to significant changes observed in solute chemistry, certain carbonate and oxide mineral phases may be expected to form and exert control on solute chemistry at geochemical interfaces, representing zones where iron-rich, anoxic waters mix with oxic groundwater. These authigenic minerals could also have an effect on the geochemical partitioning of radionuclides, even though ferric oxyhydroxide does not appear to be an effective in situ radionuclide scavenger in the presence of organic complexing agents.

Table 4.11 Ratios of ion activity products to mineral solubility constants (log IAP/KT) for anoxic and oxidized trench leachates.[a]

Trench	Redox State	pH	Eh(mV)	Calcite	Dolomite	Siderite	Vivianite	$Fe(OH)_3$[b]
7(81)	Anoxic	7.4	-44	0.51	1.49	1.57	2.18	-0.77
	Oxidized	8.1	+402	1.11	2.70	-4.09	-15.1	2.82
19s(78)	Anoxic	6.9	25	-0.21	0.12	1.98	4.38	-0.10
	Oxidized	8.5	397	-0.34	-0.13	-6.52	-16.7	2.96
19s(79)	Anoxic	6.9	57	-0.22	0.23	1.80	3.32	0.36
	Oxidized	8.6	393	-0.27	0.16	-6.55	-17.8	2.98
19s(81)	Anoxic	6.5	-28	-0.50	-0.41	1.49	2.14	-7.38
	Oxidized	7.7	+402	0.66	1.91	-2.02	-8.38	4.07
23(81)	Anoxic	7.5	-39	0.09	1.70	1.81	1.81	-0.58
	Oxidized	8.7	+394	1.14	3.82	-5.21	-20.4	2.38
27(78)	Anoxic	6.6	17	-0.38	-0.50	2.16	6.86	-0.17
	Oxidized	3.0	557	6.53	-12.8	-7.08	-14.7	-4.65
27(79)	Anoxic	5.9	140	-0.75	-1.26	1.40	2.10	-0.10
	Oxidized	3.0	300	-6.18	-12.1	-7.19	-17.5	-9.16
27(81)	Anoxic	6.8	+17	-0.21	0.01	1.51	3.44	-0.41
	Oxidized	3.7	+400	-5.87	-11.3	-4.56	-30.4	-3.43
32(79)	Anoxic	7.5	-56	0.35	1.77	0.21	-2.40	-2.28
	Oxidized	9.0	368	0.07	2.20	-7.53	-22.2	-0.11
33L8(81)	Anoxic	6.0	-135	-0.33	-1.05	0.92	0.08	-5.83
	Oxidized	8.2	+379	1.54	2.72	-3.95	-14.0	2.96
35(81)	Anoxic	8.2	-14	1.11	3.52	1.59	0.43	1.07
	Oxidized	8.4	+399	1.28	3.87	-4.63	-18.5	2.42

[a] Calculations based on geochemical code WATEQ (Plummer et al., 1983).

[b] Amorphous phase.

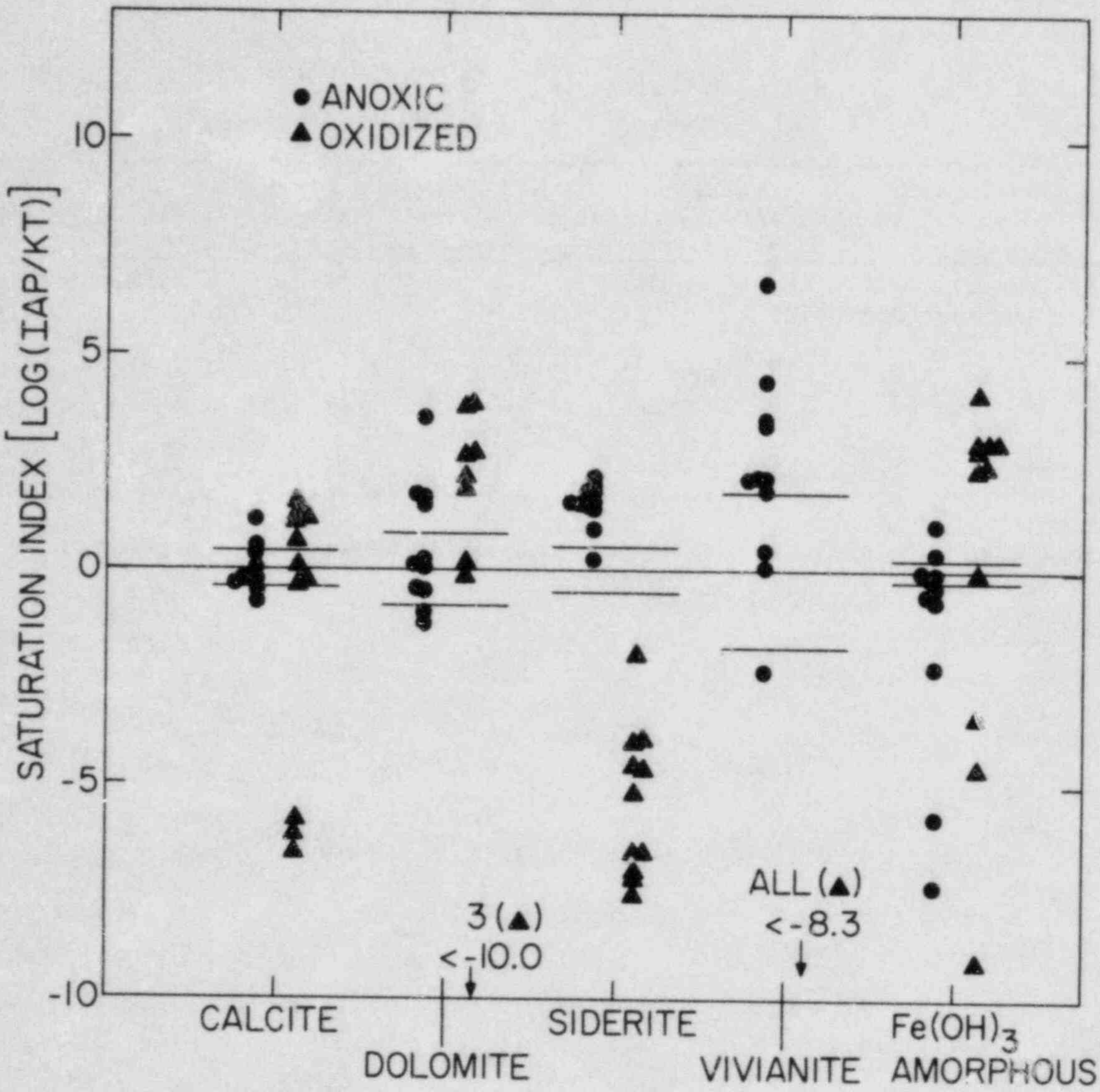


Figure 4.20. Calculated ion activity products for the major solutes (IAP) in anoxic and oxidized trench leachates compared with solubility products (K_{sp}) of selected mineral phases. The comparisons are made in terms of saturation index [log(IAP/KT)]. The data points represent calculated saturation indices for anoxic and oxidized leachates.

4.2.2 Role of Organic Complexants in Waste Migration

Organic chelating agents such as EDTA, NTA, and DTPA are known to increase the solubility of many metals due to the formation of stable metal complexes. As a result, complexation significantly affects the sorption behavior as well as the mobility of radionuclides (Swanson, 1983). Complexing by EDTA is shown to be an important mechanism for increased mobility of some radionuclides. Migration of Co-60, derived from waste disposal pits at Oak Ridge, has been attributed to complexing with EDTA (Means et al., 1978).

Since the trench leachates at Maxey Flats are known to contain appreciable concentrations of organic complexing agents as well as chelating agents (Tables 3.12 and 3.13) and some of the radionuclides such as Co-60 and the Pu isotopes are believed to be present as mobile radionuclide complexes, several experiments were conducted at BNL during the course of this study to provide some generic information on the role of organic complexing agents on geochemical cycling of radionuclides present in anoxic trench leachates as they migrate along groundwater flowpaths. Specifically, experiments were designed to evaluate: (a) the stability of radionuclide complexes with EDTA and NTA under anoxic trench conditions; (b) the effect of organic complexing agents on radionuclide sorption and mobility; and (c) the effect of chelating agents on radionuclide scavenging by authigenic mineral precipitates such as ferric oxyhydroxide.

4.2.2.1 Stability of Radionuclide Complexes

Laboratory experiments were conducted to evaluate the stability of metal complexes in a strongly reducing sulphide-bearing environment. Briefly, the experimental procedures, as described by Czyscinski and Kinsley (1982), were as follows: a simulant of trench leachate 32 and some organic material were placed in an environmental chamber along with disaggregated Nancy shale. The sealed environmental chamber was equipped with pH and sulphide electrodes to monitor development and evolution of anoxic conditions as a consequence of bacterial degradation of the organic material. The pH was kept at approximately 7 by adding 1N H_2SO_4. For the majority of experiments, the system was allowed to reach the lowest redox state possible, as indicated by the Eh and sulphide electrodes. At this point, the tagged stock solution of trace metal complex was injected through the septum port to give the initial concentrations listed in Figure 4.21. The solution was sampled periodically and the filtered sample analyzed to determine the relative amounts of metals in solution at different time periods.

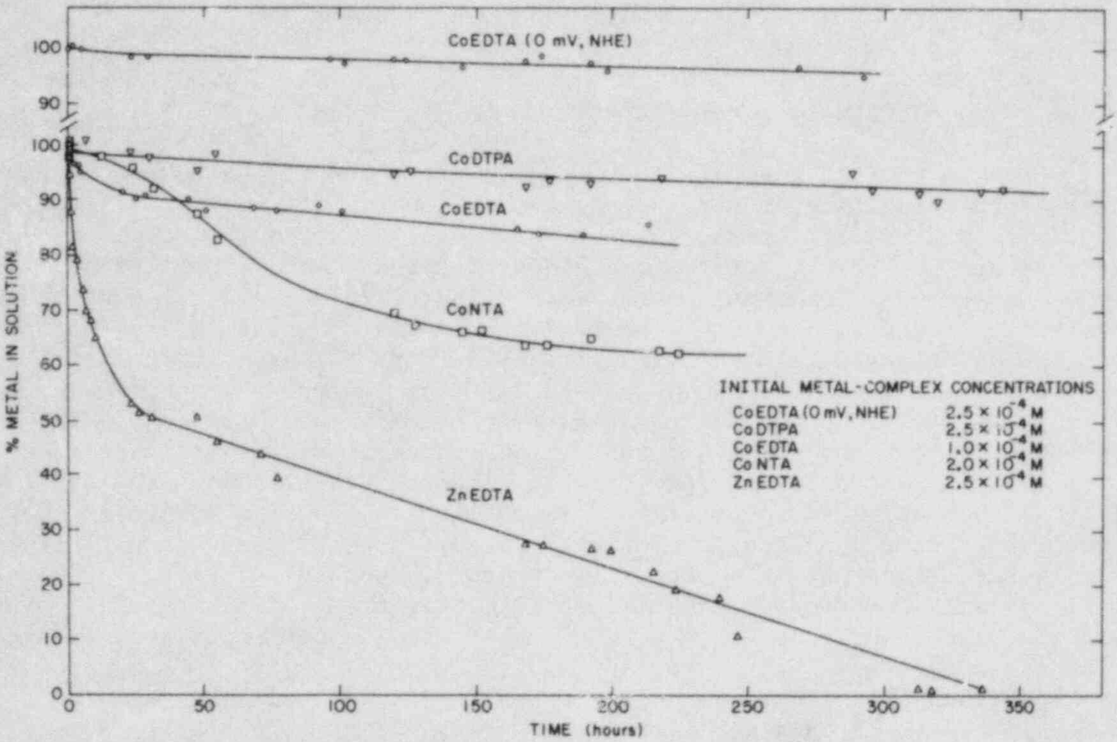


Figure 4.21. Percent metal in solution vs time for Co and Zn chelate stability experiments. The Eh for the experiments are approximately -200 mV, SHE for ZnDTPA, CoNTA, CoDTPA, and -250 mV, SHE for CoEDTA, except where indicated. The pH was maintained at approximately 7. A simulant of Maxey Flats trench leachate 32 and Nancy shale were used in the experiments.

Five experiments were performed, four under strongly reducing redox conditions (approx. -200 mV and -250 mV, SHE) and one under relatively more oxidizing conditions (approx. 0 mV, SHE). Low redox conditions were considered for CoEDTA, NTA, and DTPA stability experiments, and the more oxidizing condition for an additional CoEDTA experiment. ZnEDTA stability was also investigated under the most reducing conditions.

Figure 4.21 illustrates the stability of CoEDTA, CoDTPA, CoNTA, and ZnEDTA complexes under strongly reducing conditions and that of CoEDTA under oxidizing conditions. As reported by Czyscinski and Kinsley (1982), cobalt shows initially a rapid decrease in metal ion concentration in solution followed by an asymptotic approach to steady state conditions. The observed decreases may simply be due to sorption of the uncomplexed metal onto the shale. The decrease in cobalt concentration for the NTA system was greater than that for the EDTA system. This may be due to the fact that either NTA is much more biodegradable or that the extent of complex formation is not as much as in the case of EDTA. Neither of these experiments showed the precipitous drop in trace metal concentration under strongly reducing conditions shown by Zn and Cu in the work of Reddy and Patrick (1977).

After apparent steady state conditions were established in the chamber containing the CoEDTA complex, an aqueous solution of manganese chloride was added, such that the cobalt and manganese were in equimolar concentrations. This was done to test whether cobalt would be displaced by manganous ion and subsequently removed from solution by shale.

The results shown here in Figure 4.22 indicate that cobalt complexes with EDTA and NTA persist in strongly reducing, anaerobic environments typical of burial trenches, where anoxic conditions develop. The shale is relatively ineffective in removing cobalt from solution in the presence of EDTA, indicating that cobalt is complexed with EDTA and that the complex is stable under anaerobic conditions, even in the presence of manganous ion.

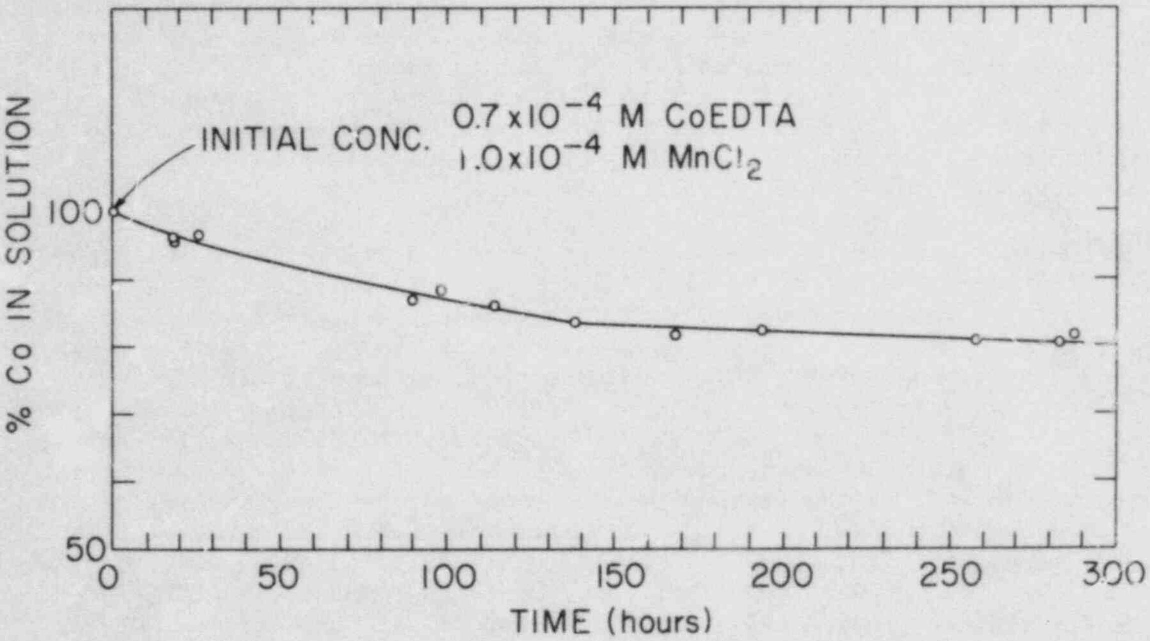


Figure 4.22. CoEDTA stability after addition of $MnCl_2$ under reducing conditions. A simulant of Maxey Flats trench leachate 32 and Nancy shale were used in the experiments.

4.2.2.2 Radionuclide Sorption and Mobility

A series of scoping experiments were performed to ascertain the effect of EDTA on radionuclide sorption. Other organic substances included in this study, which are known to act as potential complexants, were a decontaminating agent, oxalic acid, and solvents used as extractants, which had been identified in trench waters. Maxey Flats well water UB1-A, which is relatively free of the organic substances found in the disposal trench waters, was used in these experiments. Another set of experiments was performed to determine the effect of EDTA on retention of radionuclides by various commonly encountered soil forming minerals. Clay minerals, particularly the expandable 2:1 layer silicates, exhibit the ability to adsorb organic molecules in the interlayer sites (Grim, 1968). Samples of the major classes of clay minerals were used along with limonite, a common iron bearing soil component. Distribution coefficients were measured in the absence and presence of EDTA. Details of the laboratory procedures used in the two sets of experiments are given elsewhere (Czyscinski and Weiss, 1981).

The results of the sorption experiments displayed in Figure 4.23, showing the effect of varying EDTA concentrations on sorption of Cs-137, Am-241, Co-60, and Sr-85 by Maxey Flats shale, indicate that both the presence of EDTA and its concentration level affect the extent of sorption for most radionuclides studied. In the case of Cs-137, the sorption coefficient remains unaffected at $\approx 5 \times 10^3$ mL/g in the 0-100 mg/L EDTA concentration range, indicating that EDTA does not exert any control on the sorption of Cs-137. In contrast, both Am-241 and Co-60 exhibit a drastic drop in K_d values with increasing EDTA concentrations. The sorption coefficient of 2×10^6 mL/g for Am-241 in EDTA-free system drops by approximately three orders of magnitude to a value of 3×10^3 mL/g in 100 ppm EDTA-spiked system. Co-60 shows a similar sorption behavior with increasing EDTA concentrations. Sr-85, on the other hand, exhibits a decline from an initially low value of 4×10^0 mL/g in EDTA-free system to 2×10^0 in EDTA-spiked system. It should be noted the the extremely low K_d value (1×10^0 mL/g) for Co-60 measured in 100 ppm EDTA-spiked system indicates that a major part of cobalt is present as a non-sorptive EDTA complex and that partitioning of the radionuclide between the solid and the liquid phases is practically neglible.

The effect of other complexing agents such as oxalic acid, tributylphosphate (TBP), tetrahydrafuran (THF) , and MIBK [all these organic compounds were also found in the trench leachates] on the sorption of Am-241, Co-60, Cs-134, Cs-137, and Sr-85 by Maxey Flats shale was also investigated. The sorption data shown in Figure 4.24 indicate that, like EDTA, all four complexing agents investigated do not appear to have any effect on the sorption behavior of the cesium isotopes, Cs-134 and Cs-137. Am-241, however, appears to be the most affected in the presence of added organic compounds, with tributylphosphate showing the maximum effect on the sorption coefficient of the presence of 100 ppm EDTA, however, the Am-241 sorption coefficient decreased from 10^6 mL/g (EDTA-free) to 3×10^3 mL/g. This value is still more than an order of magnitude greater than that observed in the presence of TBP, indicating the high complexing capacity of EDTA for Am-241 compared to that of TBP. Co-60 sorption appears to be unaffected, except when oxalic acid is present which shows a slight decrease in K_d, indicating limited formation of a cobalt-oxalic acid complex. Sr-85 shows a slight decline in sorption coefficient when TBP, THF, and MIBK are present. This is comparable to that observed for EDTA-spiked system.

In summary, cesium sorption remains unaffected in the presence of the organic substances studied. Compared to other radionuclides, Am-241 sorption was influenced by all the complexing agents, with EDTA being the most effective. In the case of cobalt, however, only EDTA exerted a strong effect on its sorption behavior. Sr-85 exhibited a slight decline in the sorption coefficients in the presence of all organic substances, except oxalic acid.

Lower sorption coefficients observed in the presence of complexing agents can be attributed to formation of stable radionuclide complexes. Americium appears to form complexes with all the organic substances studied, however, the extent of complexation is most pronounced in the case of EDTA. Similarly, cobalt also appears to form a strong complex with EDTA. The results further show that, even in the presence of EDTA, both cobalt and americium are removed from solution by shale, indicating that although their potential for sorption is considerably reduced some sorption is still possible.

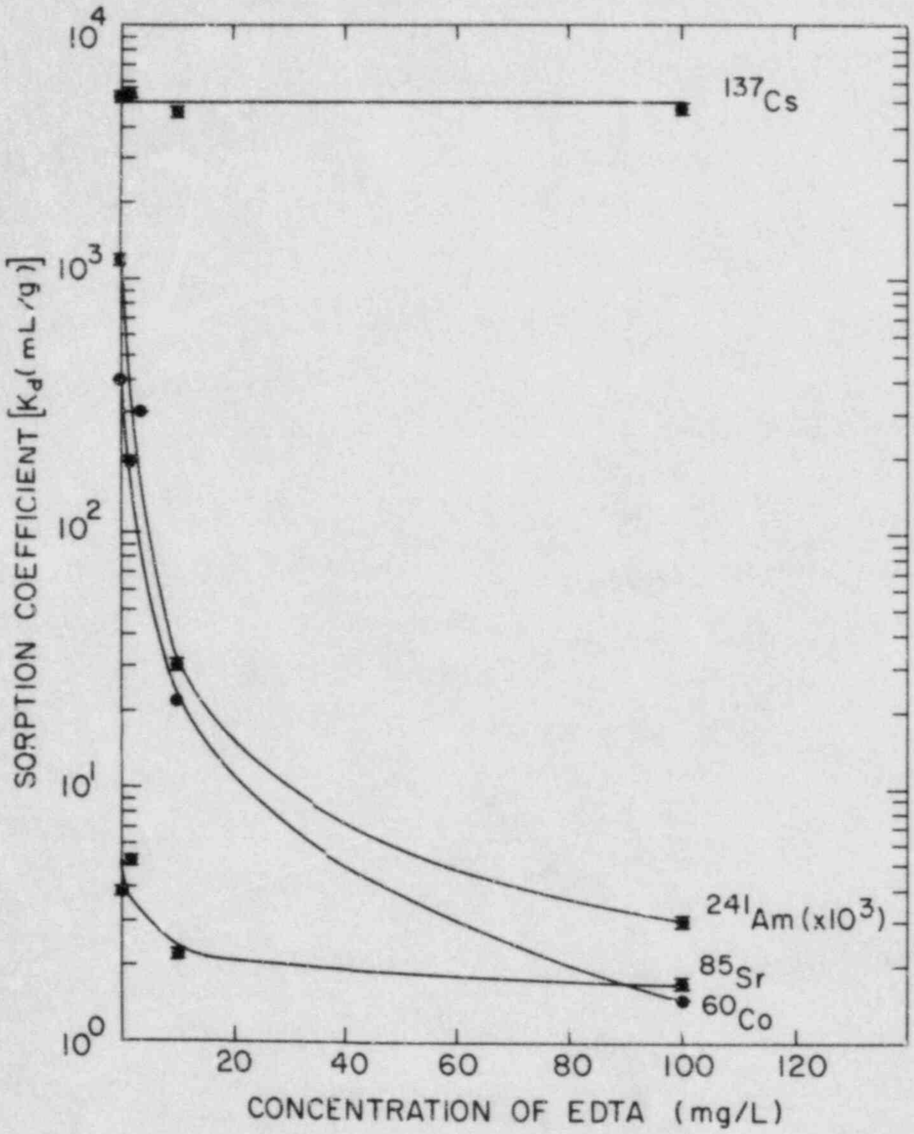


Figure 4.23. Effect of varying EDTA concentrations on the sorption behavior of Am-241, Co-60, Sr-85, and Cs-137. Maxey Flats well water UB1A and Nancy shale were used in the experiments.

Another study was performed to determine the effect of EDTA on retention of radionuclides by various commonly encountered soil forming minerals. Samples of the major clay minerals were used along with limonite, a common iron-bearing soil component. Radionuclide partitioning was measured with and without the addition of EDTA to the well water-mineral system.

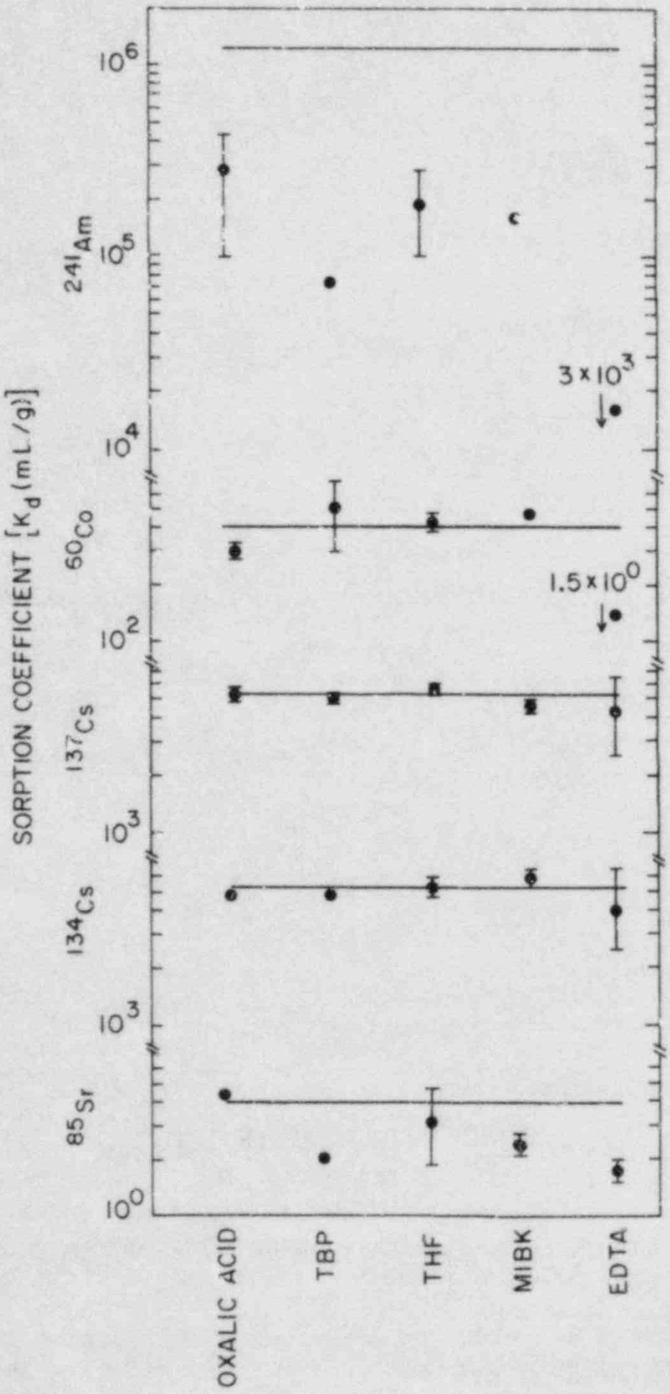


Figure 4.24. Effect of organic complexants oxalic acid, tributylphosphate (TBP), tetrahydrafuran (THF), MIBK, and EDTA on the sorption behavior of Am-241, Co-60, Cs-134, Cs-137, and Sr-85. Maxey Flats well water UB1-A and Nancy shale were used in these experiments. Solid lines represent radionuclide sorption coefficients in the absence of organic constituents.

Figure 4.25 shows that the strontium, cobalt, and cesium sorption coefficients for shale and illite are similar. This is not surprising considering that the Maxey Flats shale used in this study is primarily illitic. Furthermore, as discussed earlier, the presence of EDTA does not affect the sorption behavior of cesium and strontium, but exerts a pronounced effect on cobalt. In EDTA-free systems, both limonite and vermiculite exhibit comparable sorption capacities for most radionuclides. When EDTA is added, however, both cobalt and americium show a significant decrease in their sorption coefficients. In contrast, cesium and strontium sorption appears to be unaffected. This observation is in agreement with our earlier hypothesis that alkali metals show relatively little affinity towards the formation of complexes with EDTA while both americium and cobalt form strong complexes.

Kaolinite appears to be the least effective in removing radionuclides from solution. This is not surprising considering that, among the common clay minerals, kaolinite has the lowest sorption capacity.

Montmorillonite is a notable exception in that both americium and cobalt, radionuclides which form strong complexes with EDTA, do not appear to be significantly affected in terms of their sorption behavior when EDTA is added to the system. It is quite conceivable that because of the expandable character of the montmorillonite type clays, the radionuclide-EDTA complexes are incorporated in the interlayer sites of the clay structure. In fact, adsorption of organic molecules, particularly polar molecules, by montmorillonite type expandable 2:1 layer silicates is well known (Grim, 1968). Therefore, since the expandable clays have the ability to remove radionuclide complexes from solution, our observations of substantial sorption of americium and cobalt by montmorillonite in the presence of EDTA are not surprising.

4.2.2.3 Radionuclide Scavenging by Authigenic Ferric Oxyhydroxide

Laboratory experiments were conducted to determine the role of strong organic complexants such as EDTA on radionuclide scavenging by ferric oxyhydroxide, simulating a geochemical discontinuity where iron- and organic-rich anoxic leachates encounter an oxidizing environment.

Based on the results of oxidation experiments conducted on several anoxic trench leachates (Table 4.10), it is clear that almost all trench leachates upon oxidation exhibit removal of dissolved iron from solution, as a result of ferric oxyhydroxide precipitation. However, the radionuclide data in Table 4.9 indicate that coprecipitation or scavenging of Co-60, Cs-137, and Sr-85 by the resultant precipitate is minimal. Among the radionuclides studied, Cs-137 is removed the least from solution, followed by Co-60 and Sr-85. The maximum removal of Sr-85 and Co-60 is observed in leachate 33L8 with values approaching 67% and 63% of the initial amounts present. The lack of substantial removal of dissolved radionuclides upon oxidation of trench leachates, even in the presence of a ferric oxyhydroxide precipitate, can be attributed to complexation of radionuclides with chelating agents, considering that relatively large concentrations of dissolved organic carbon are present. As discussed earlier, some organic chelating agents such as NTA, DTPA, and

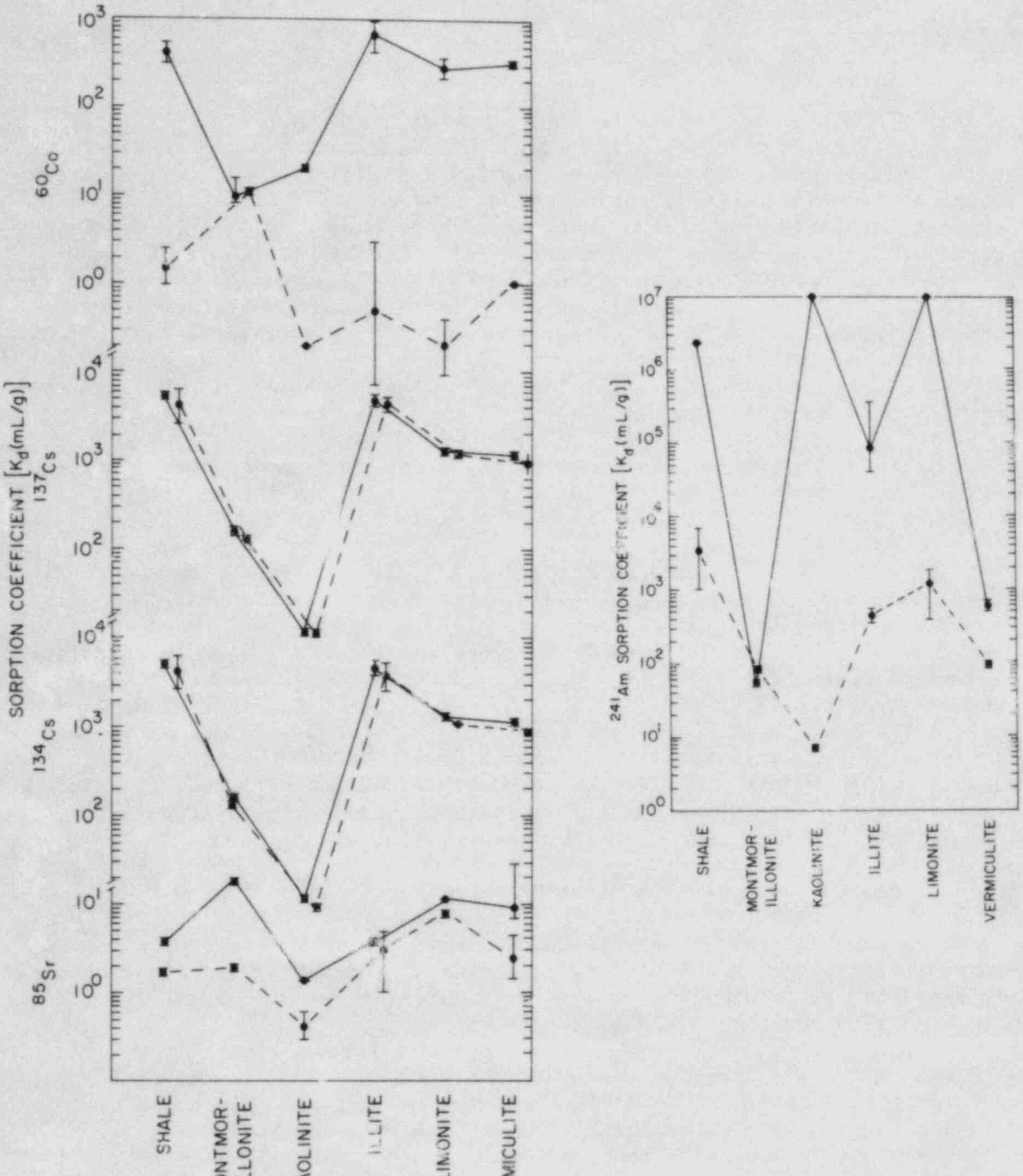


Figure 4.25. Effect of EDTA (dashed line) on partitioning of Am-241, Co-60, Cs-134, Cs-137, and Sr-85 by common soil forming minerals, including limonite. Solid line represents EDTA-free systems. Sorption data for Nancy shale are also included. In these sorption experiments, conducted with Maxey Flats well water UB1-A, the initial EDTA concentration was 100 ppm EDTA.

EDTA and several organic complexants have been reported in these trench waters. Table 3.13 shows that greater than 50% of the total hydrophilic organic compounds present in leachate 33L8 consist of complexing agents. In an earlier report (Pietrzak et al., 1983), we presented data on the oxidation behavior of West Valley trench leachate 8 as a function of time, showing that, even though ferric oxyhydroxide precipitation occurred upon air oxidation of the anoxic leachate, coprecipitation of dissolved radionuclides was minimal. Cleveland and Rees (1981) made a similar observation for total dissolved Pu in Maxey Flats trench leachates, where plutonium is reported to exist primarily as complexes of the tetravalent ion with strong organic ligands such as EDTA. Only partial precipitation of dissolved plutonium by ferric oxyhydroxide was reported. Work at PNL also shows generally good correlation between Pu and Co-60 and EDTA, and between Sr-90 and Cs-137 and carboxylic acids in water samples from experimental trench sections located in the vicinity of trench 27 (Kirby et al., 1984). Polzer et al. (1984) have also reported the occurrence of Pu-EDTA complexes in trench leachate 19s. These studies indicate that complexing by EDTA appears to be a potentially important mechanism that increases mobility of Co-60 and the Pu isotopes.

In our oxidation experiment, we specifically chose EDTA to determine whether strong organic complexants were indeed responsible for the observed lack of removal of dissolved radionuclides by ferric oxyhydroxide in oxidized trench leachates. For this purpose, Maxey Flats trench leachate 33L8, the only trench leachate which exhibited substantial removal of Co-60 and Sr-85 from solution upon oxidation, was selected. The leachate sample was spiked with varying amounts of disodium EDTA: 0 ppm, 0.14 ppm, 1.4 ppm, and 14.0 ppm. The spiked leachate samples were exposed to air for a period of two weeks. Following complete oxidation, the samples were analyzed for Co-60, Sr-85, and Cs-137 remaining in solution.

The results show that increasing amounts of Co-60 remain in solution upon oxidation of leachate samples spiked with increasing amounts of EDTA, with the maximum Co-60 solubilization occurring at a disodium EDTA concentrations of ≈2 ppm (Figure 4.26). No significant decrease in the removal of Sr-85 and Cs-137 was observed with increasing amount of EDTA in solution. It is interesting to note that, in our earlier experiments (Figure 4.25), limonite, which is chemically and mineralogically similar to ferric oxyhydroxide, also exhibited lack of removal of Co-60 in the presence of EDTA. However, Sr-85 and the cesium isotopes, Cs-134 and Cs-137, remained unaffected. These findings confirm our earlier hypothesis that, at least for Co-60, complexation of radionuclides with complexing agents such as EDTA prevents their removal from solution by ferric oxyhydroxide. This observation indicates that organic complexing agents play an important role in the geochemical cycling of radionuclides in Maxey Flats trench leachates. This is further substantiated by our findings of decreased radionuclide sorption on Maxey Flats shale and some common soil forming minerals, especially the sorption of cobalt and americium in the presence of EDTA and tributylphosphate.

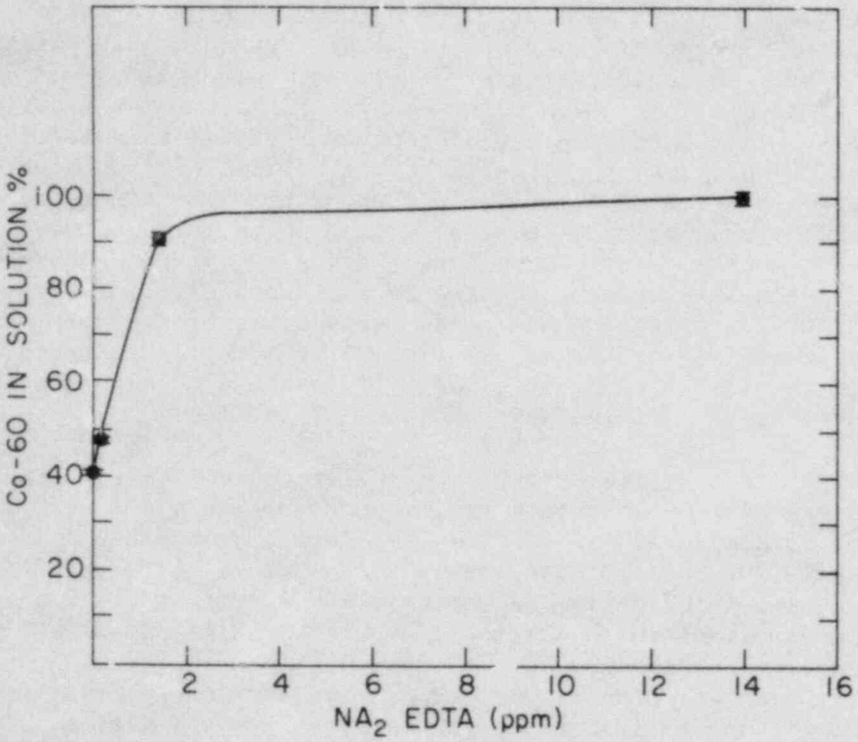


Figure 4.26. Co-60 remaining in solution upon oxidation of anoxic trench leachate 33L8 spiked with varying amounts of disodium EDTA.

4.2.3. In Situ Leachate Migration

4.2.3.1. Experimental Trench Area

An experimental facility was established on the disposal site to investigate in situ leachate migration by subsurface routes in the vicinity of burial trench 27. The experimental area consisted of an experimental trench excavated parallel to trench 27 in 1979 for the purpose of intercepting leachate flowing from the burial trench area. Subsequently, a series of inert atmosphere wells were installed in the same area to facilitate sampling of leachates without exposure to air (Figure 4.27).

The results of inorganic and radionuclide constituents in the water samples taken from trench 27 and experimental trench sections T2E, T3E, T4E, and T5 by BNL in 1979 are given in Table 4.12. Analysis of the data indicates leachate migration by subsurface routes in the vicinity of burial trench 27. Initial observations made at the site during excavation of the experimental trench indicate that water flowed into three sections of the experimental trench and that the radionuclide concentrations in these waters were similar to that of trench leachate 27 (Kirby et al., 1984).

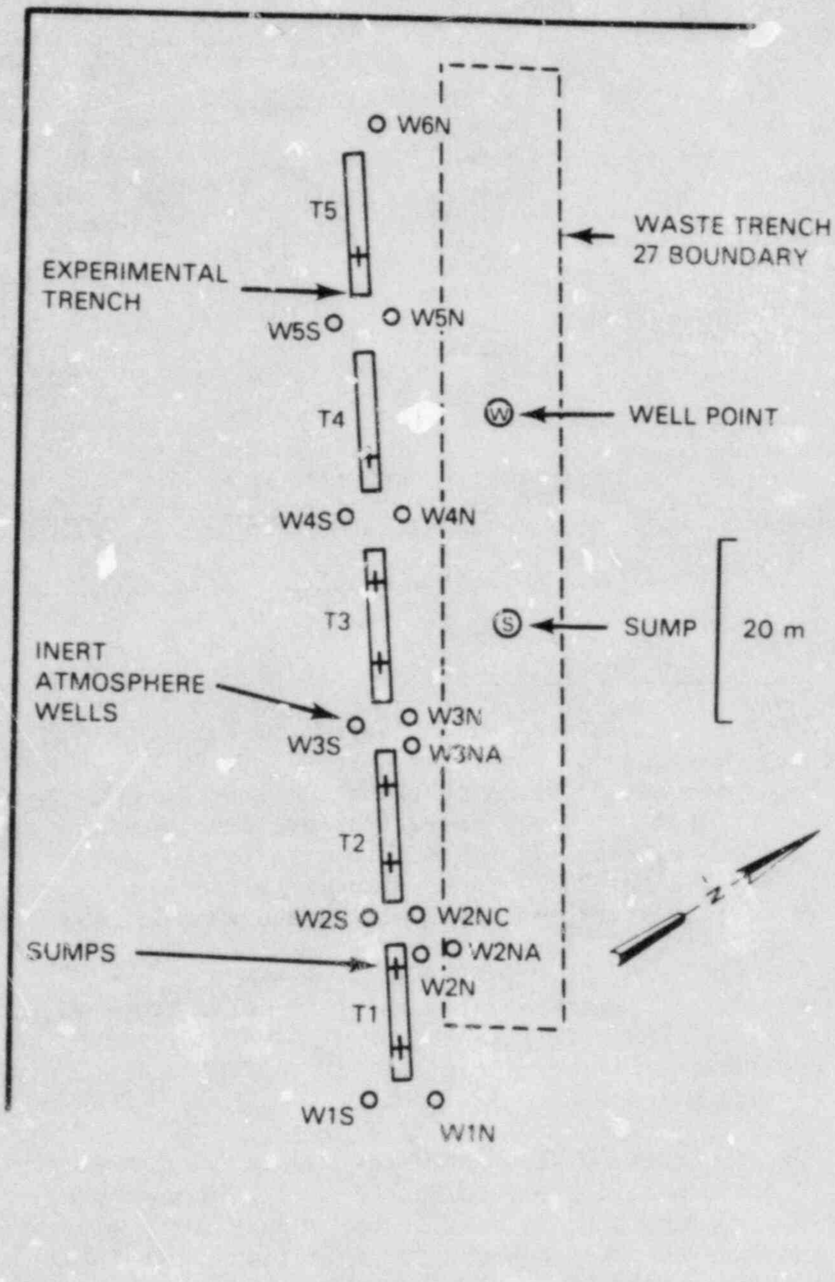


Figure 4.27. Maxey Flats experimental area, consisting of the experimental trench sections and inert atmosphere wells near waste trench 27.

Table 4.12. Concentration of dissolved constituents in trench 27 and experimental trench leachates[a]

Constituents	Concentration (mg/L)				
	27	T2E	T3W	T4E	T5
Anions					
Alkalinity (as $CaCO_3$)	300	300	450	300	320
Bromide	180	180	2200	2	4100
Chloride	6100	1200	160	140	84
Nitrate (as N)	0.75	0.51	0.39	<0.05	1.4
Phosphate	<1	<1	<1	<1	<1
Silica	19	8	9	8	0.7
Sulfate	2	530	980	1500	1300
Cations					
Ammonia (as N)	60	20	9	5	<1
Barium	17	<2	<2	<2	<2
Calcium	740	380	450	610	610
Iron-total	1400	1.3	1.3	0.5	0.2
Iron-ferrous	1365	1.0	0.1	b	b
Lithium	2.3	<0.5	<0.5	<0.5	<0.5
Magnesium	720	160	95	95	130
Manganese	190	3.5	2.7	1.1	0.2
Potassium	100	35	26	17	32
Sodium	770	530	910	280	1200
Strontium	7	8	7	6	8
Others					
Dissolved Organic Carbon	500	120	15	29	14
Dissolved Inorganic Carbon	74	70	120	50	90

[a] Leachates sampled by BNL in October-November 1979 (Czyscinski and Weiss, 1981).

[b] Not determined.

Trench 27--Source of Contaminants

The radionuclide data given in Table 4.13 and displayed in Figure 4.28 show that (a) elevated concentrations of H-3, Sr-90 and Pu-isotopes are present in the experimental trench sections and that Am-241, Cs-137, and Co-60 were not detected; (b) the concentration levels of both H-3 and Sr-90 in waste trench 27 and experimental trench sections follow the sequence 27 > T2E > T3E > T4E > T5; and (c) the Pu isotopes also exhibit a similar distribution pattern in the trench waters, except that T3W shows a slightly higher concentration than T2E.

Non-radioactive constituents such as K^+, Cl^-, SiO_2, NH_4^+, and dissolved organic carbon displayed in Figure 4.29 also show similar distributions to those of the radionuclides, except that Cl^- and K^+ are relatively enriched in T5 compared to T3W and T4E.

The distributions of free chelating agents such as EDTA and DTPA show the presence of both chelating agents in trench 27 (Figure 4.30). However, free EDTA does not appear to be present in the experimental trench sections. Free DTPA was found to be present above the detection limit in all experimental trench sections, presumably derived from trench 27.

Table 4.13. Concentrations of radionuclides in trench 27 and experimental trench leachates[a]

Radionuclide	Concentration [pCi/L (±2σ%)][b]				
	27	T2E	T3W	T4E	T5
H-3	5.1×10^{9} (<1)	6.7×10^{8} (<1)	3.7×10^{7} (<1)	1.5×10^{5} (1.1)	1.7×10^{4} (3.1)
Sr-90[c]	1.5×10^{5} (10)	1.9×10^{4} (10)	2.3×10^{2} (10)	1.8×10^{1} (38)	3.5×10^{1} (27)
Pu-238[c]	2.6×10^{4} (10)	6.8×10^{1} (10)	1.6×10^{2} (10)	2.2×10^{1} (10)	4.9×10^{0} (18)
Pu-239,240[c]	2.4×10^{3} (10)	9.3×10^{-1} (20)	1.7×10^{0} (34)	8.9×10^{-1} (50)	2.5×10^{-1} (100)
Am-241	4.7×10^{3} (3.0)	$<1\times10^{1}$	$<1\times10^{1}$	$<1\times10^{1}$	$<1\times10^{1}$
Cs-137	2.2×10^{3} (3.2)	$<1\times10^{2}$	$<1\times10^{2}$	$<1\times10^{2}$	$<1\times10^{2}$
Co-60	4.0×10^{3} (2.6)	$<2\times10^{2}$	$<2\times10^{2}$	$<2\times10^{2}$	$<2\times10^{2}$

[a] Leachates sampled by BNL in October-November 1979 (Czscynski and Weiss, 1981).
[b] The number in () represents 2σ% counting uncertainty.
[c] Analysis performed by LFE Laboratories, Richmond, California.

Based on the distributions of H-3, Sr-90 and Pu isotopes and several non-radioactive constituents such as K^+, Cl^-, NH_4^+, DOC, SiO_2, and DTPA in waters sampled from waste trench 27 and experimental trench sections, one can conclude that there is sufficient evidence of leachate migration by subsurface routes and that the contaminants in the experimental trench sections are derived from waste trench 27. The observation that distributions of most contaminants in waste trench 27 and experimental trench sections follow the sequence 27 > T2E ≥ T3W > T4E > T5 in terms of their concentration levels indicates that the contaminant plume moves preferentially in a southerly direction towards T2E and T3W, both representing the eastern section of the experimental trench facility.

In 1980, the inert atmosphere wells were installed and subsequently sampled along with the experimental trench sections and waste trench 27. Figures 4.31 and 4.32 show the distributions of H-3, Sr-90, Pu-total, and Cl^- in waste trench 27, the inert atmosphere wells, and the experimental trench sections. The inert well data are solely based on samplings conducted by PNL, whereas the experimental trench data are based on both BNL and PNL investigations.

The distribution profiles show that for contaminants, such as H-3, Sr-90, Pu-total, and Cl^-, leachate 27 exhibits the highest concentrations, indicating trench 27 to be the source. The comparably high concentrations of H-3, Sr-90, Pu-total, and Cl^- in experimental trench sections T1 and T2, and inert wells W2NA and W3NA indicate excellent subsurface communication in this area of the experimental facility and with trench 27. The contaminant profiles further indicate relatively poor communication between trench 27 and the extreme western (T5 and W5N) and eastern (W1N) sections of the experimental trench facility. This observation is further supported by recent PNL data (Kirby et al., 1984) indicating the absence of waste-derived EDTA from trench 27 in inert atmosphere wells W1N, W3N, and W3NA and in experimental trench sections T4 and T5.

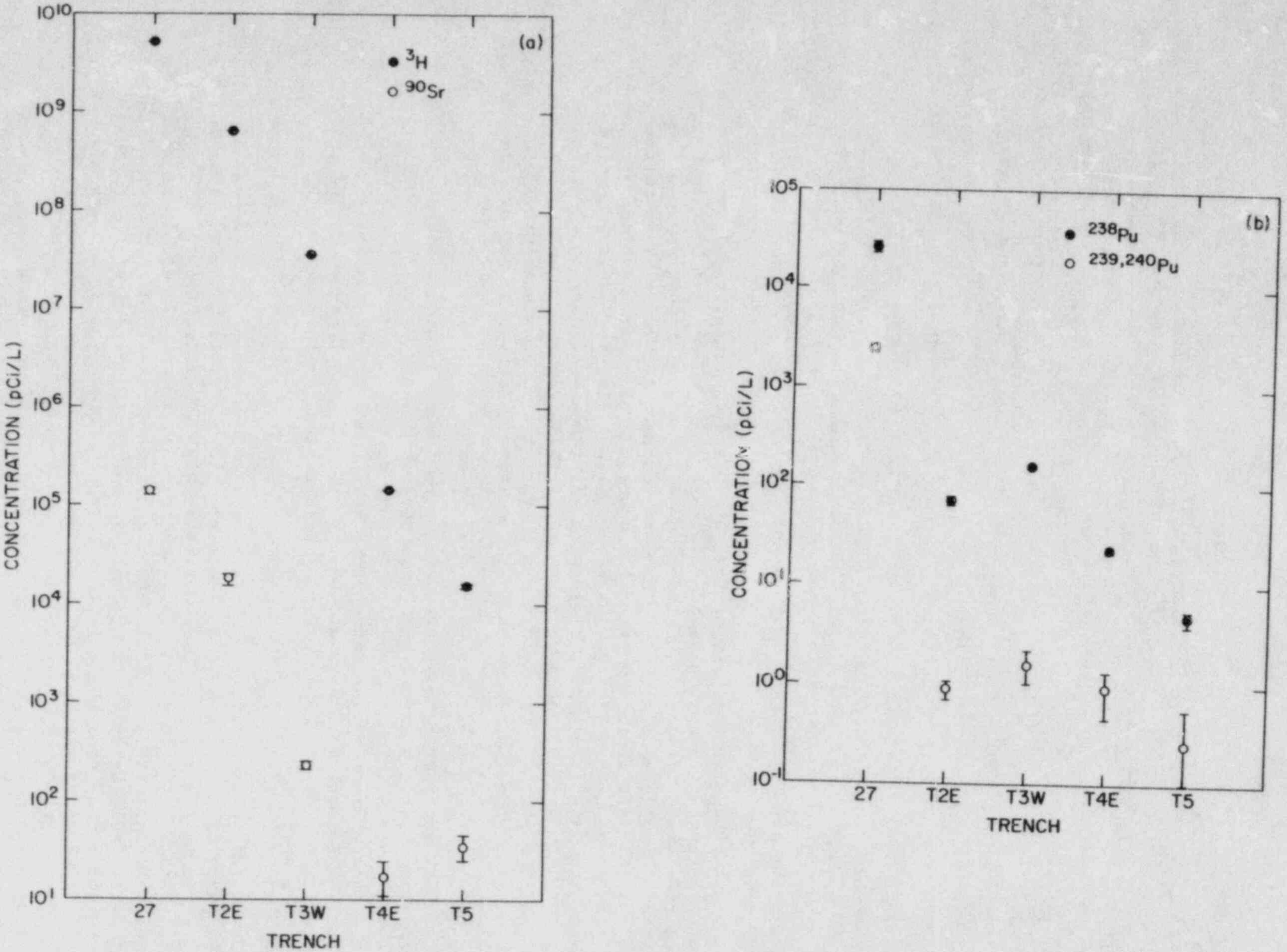


Figure 4.28. Distributions of (a) H-3 and Sr-90 and (b) Pu isotopes in waters from trench 27 and experimental trench sections.

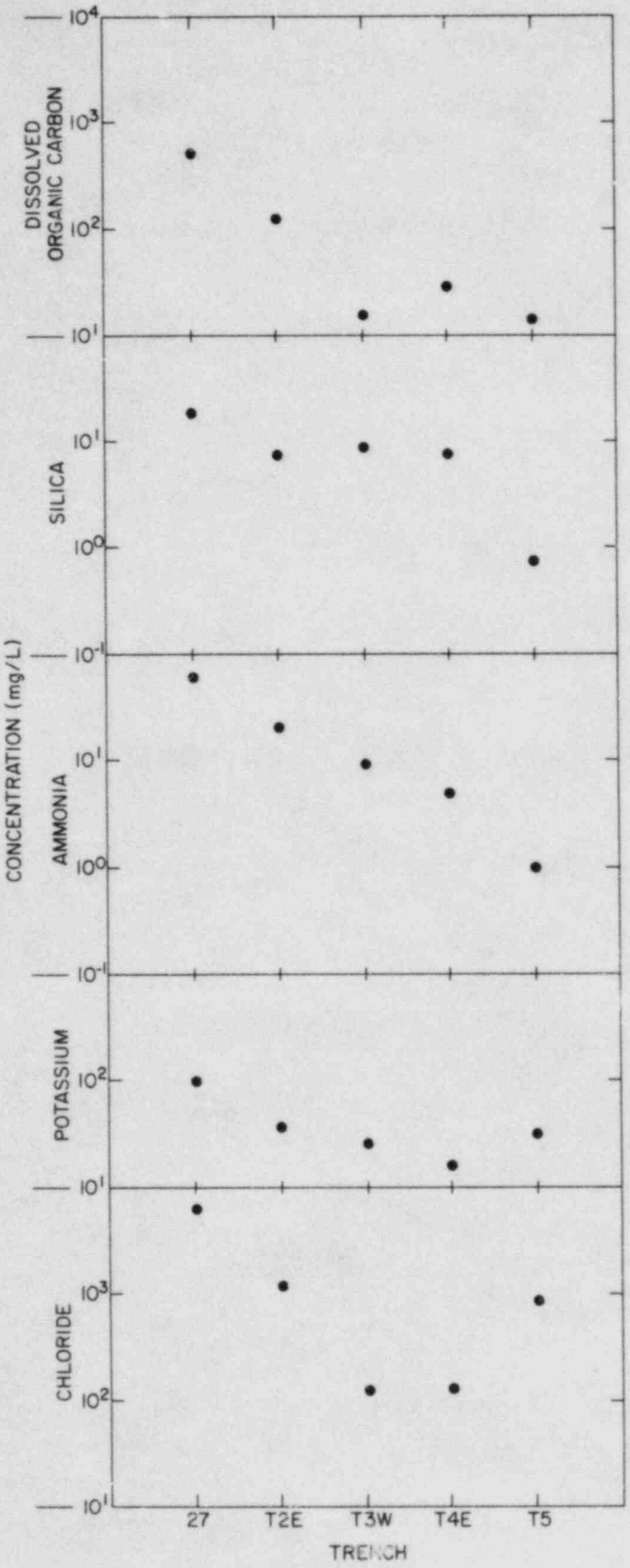


Figure 4.29. Distributions of dissolved organic carbon, silica, ammonia, potassium, and chloride in waters from trench 27 and experimental trench sections.

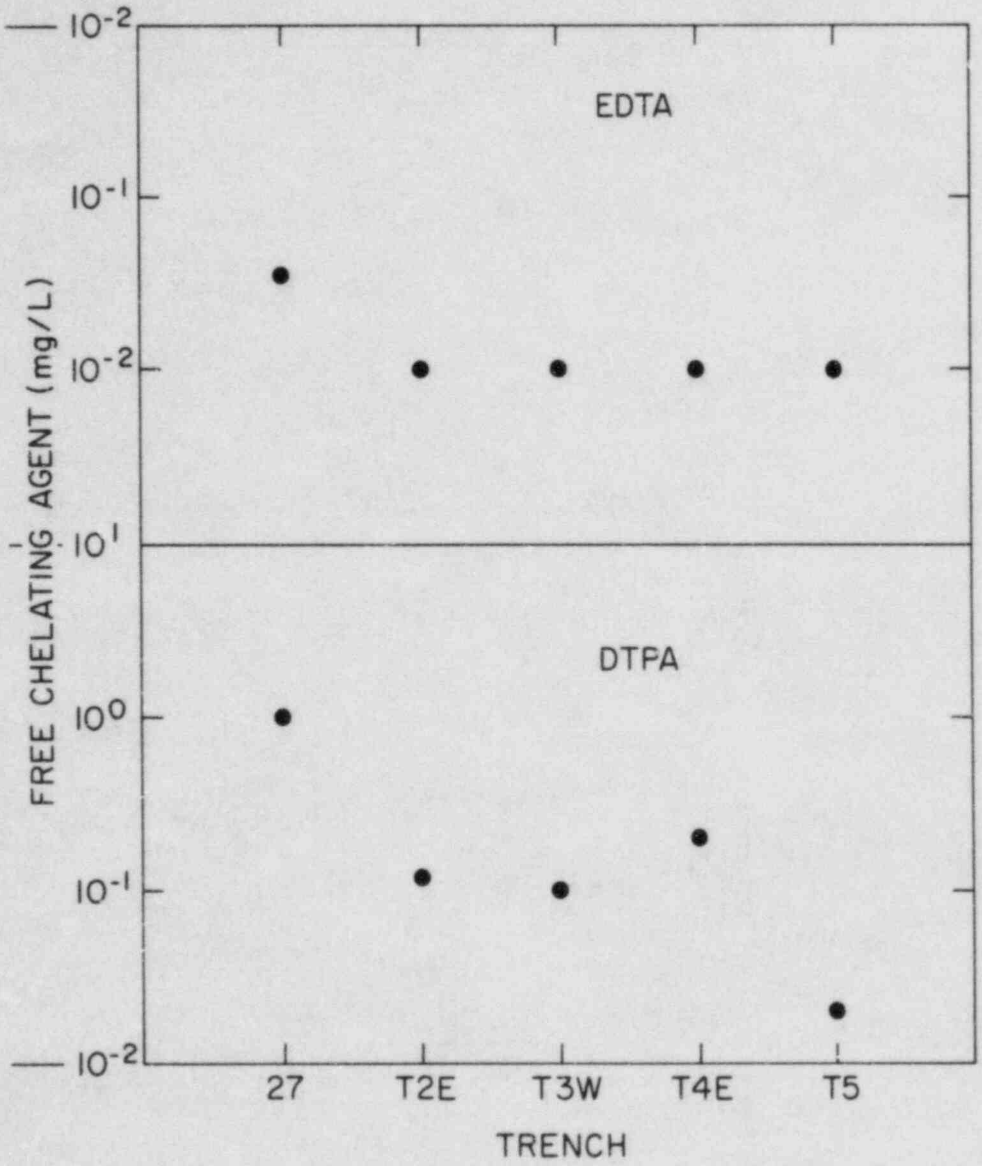


Figure 4.30. Distributions of free chelating agents EDTA and DTPA in waters from trench 27 and experimental trench sections.

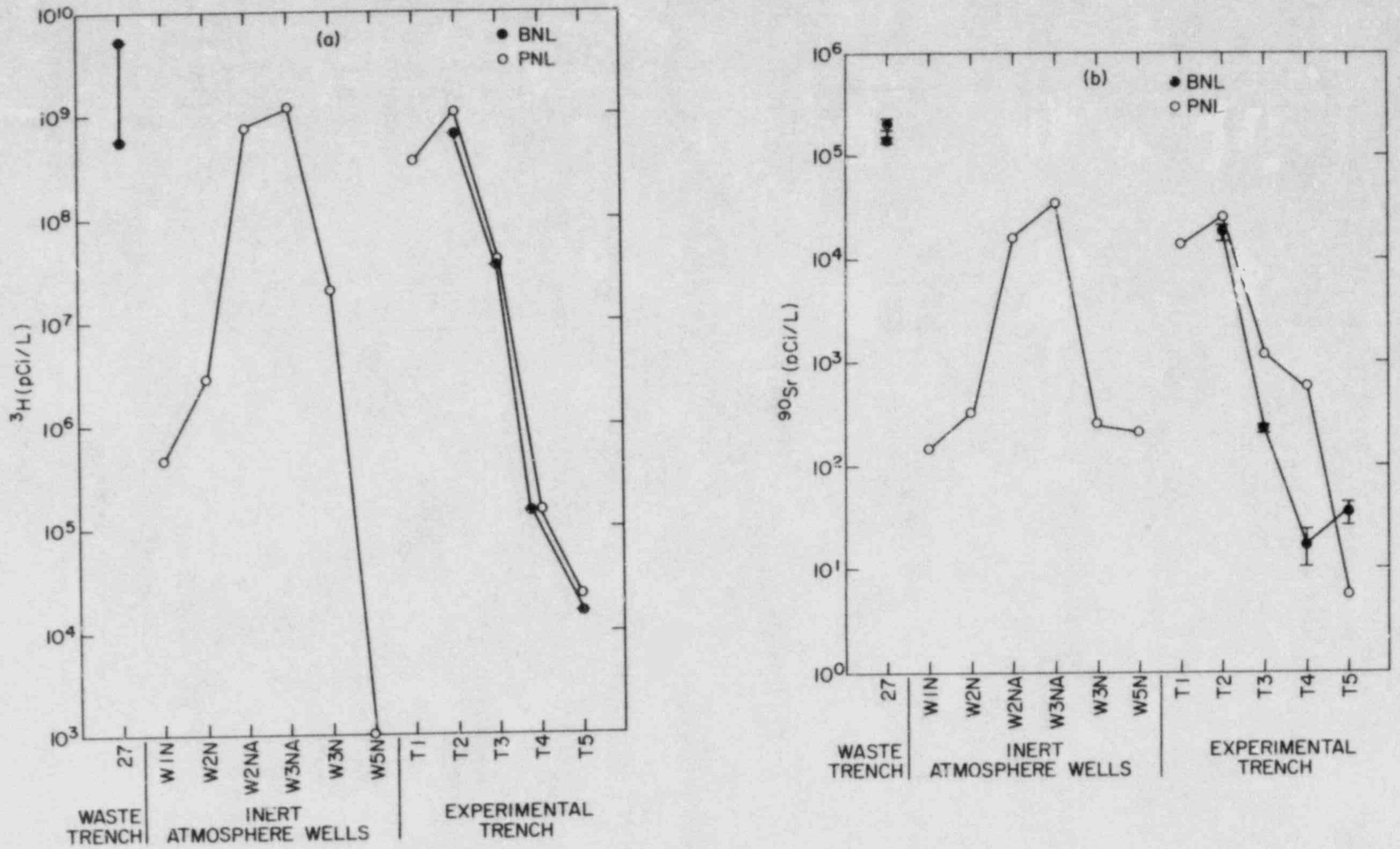


Figure 4.31. Distributions of (a) H-3 and (b) Sr-90 in waters from trench 27, inert atmosphere wells, and experimental trench sections. The range of radionuclide concentrations shown for trench 27 is based on multiple samplings conducted by BNL.

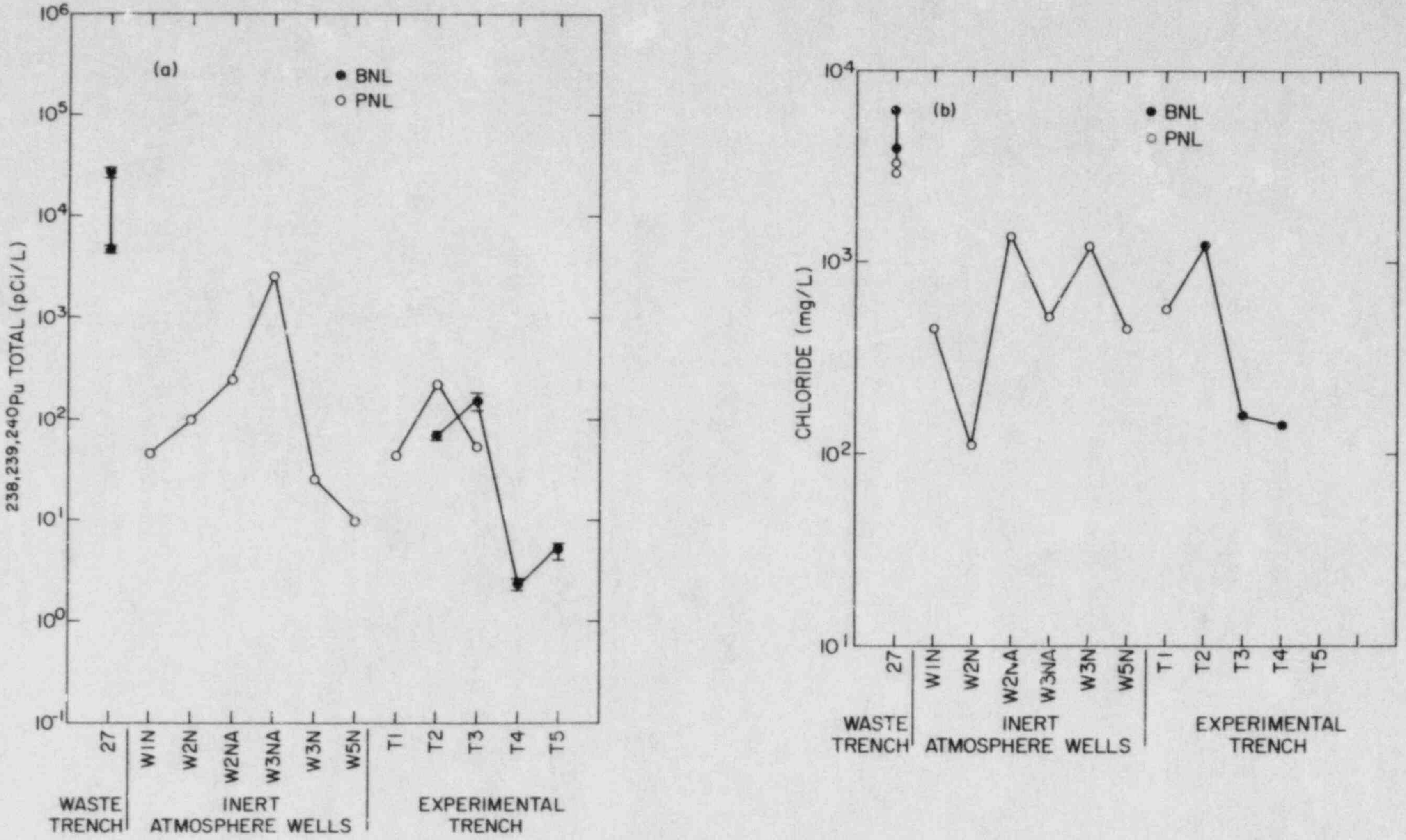


Figure 4.32. Distributions of (a) total plutonium and (b) chloride in trench 27, inert atmosphere wells, and experimental sections. The range of plutonium and chloride concentrations shown for trench 27 is based on multiple samplings by BNL.

Results of the organic analysis of trench leachates and experimental trench waters conducted by BNL are given in Table 4.14 (Weiss et al., 1982). The type of organic compounds present in the trench leachate and experimental trench sections indicate that several of these compounds are associated with buried wastes and that trench 27 is the probable source. Some of the organic compounds identified in the experimental trench sections could be associated with plastics used in the trench construction. In summary, the presence and type of organic compounds identified in the experimental trench sections further indicate subsurface communication in this area, preferentially in the direction of T2E and T3E from trench 27.

Experimental Trench--Source of Contaminants

NaBr was added as a groundwater tracer to experimental trench sections T2E, T3W, and T5 (Nowatzki, Thompson, and Wachs, 1981) to study subsurface water movement. Figure 4.33a shows the concentration levels of bromide in waters collected from trench 27 and experimental trench section T2E, T3W, T4E, and T5. The observed distribution profile indicates a substantial buildup of Br^- concentration in trench 27, presumably derived from the experimental trench sections. The observation that Br concentrations in trench 27 and experimental trench section T2E are comparable and, at the same time, significantly lower than T3W and T5 indicates excellent subsurface communication between trench 27 and T2E and relatively poor communication between trench 27 and the other sections of the experimental trench. Furthermore, the extremely low Br^- concentration observed in T4E (no bromide tracer added) compared to T3 and T5 indicates absence of subsurface communication between the experimental trench sections T4 and T5, and T4 and T3. Figure 4.33b shows the build up of Br^- in trench 27, derived from experimental trench sections, as a function of time. The plot indicates an increase in Br concentration of more than 400 ppm in a period of 2 years, after the experiment was first initiated.

Figure 4.34 shows the distribution of bromide in waste trench 27, the inert atmosphere wells, and the experimental trench sections. The average experimental trench bromide concentrations are much higher than those observed in the inert wells or trench 27, indicating the experimental trench to be the source of bromide. The low concentrations of Br^- observed in inert wells W1N and W2N relative to that of experimental trench section T1 indicates lack of flow of water in the direction of W2N and W1N from T1. The fact that W2NA exhibits a much higher concentration than that of W2N suggests that Br in W2NA is derived from trench 27 and experimental trench section T2 rather than from well W2N and also indicates practically no communication between the wells W2N and W2NA. Similarly, comparison of Br^- concentrations observed in T5 and W5N indicates lack of leachate migration in the direction of W5N from T5.

Table 4.14. Organic compounds identified in trench leachate 27 and experimental trench waters.[a]

Organic Compound	27	T2E	T3W	T4E	T5
Acidic Fraction:					
2-Methylpropionic acid	0.24				
2-Methylbutanoic acid	0.60				
3-Methylbutanoic acid	0.76				
Valeric acid	0.28				
Ethylene glycol	N.Q.[b]		N.Q.		
Diethylene glycol					
3-Methylpentanoic acid	0.45				
C6 acid[c]	0.16				
Phenol	0.23	0.06			
Hexanoic acid	0.64				
2-Methylhexanoic acid	0.24				
C8 acid	N.Q.	N.Q.			
Cresol (isomers)	0.56				
2-Ethylhexanoic acid	9.7	0.44			
C8 acid[d]	0.08				
C8 acid[d]	0.06				
Benzoic acid	0.24				
Octanoic acid	0.10				
Phenylacetic acid	0.16				
Nonanioc acid					
Phenylbutyric acid					
Phenylpropionic aicd	0.50				
Polyethylene glycol	N.Q.				
Phenylhexanoic acid	N.Q.				
Toluic acid					
Dioctyl adipate			N.Q.		
Di-isooctyl pthalate			N.Q.		
Neutral Fraction:					
p-dioxane		N.Q.	N.Q.		
Methylisobutyl ketone	1.8				
Toluene	0.56				
Xylene					
Cyclohexanol					
Dibutyl ketone					
2-Ethyl 1-hexanol	0.17				
Diethylene glycol diethyl ether	N.Q.				
Fenchone	N.Q.				
Triethyl phosphate	0.29				
Camphor	N.Q.				
Naphthalene	0.06				
Tributyl phosphate					
Phthalate ester					
2-butanone					N.Q.
Tetrahydrofuran		N.Q.		N.Q.	N.Q.
Cyclohexanone		N.Q.		N.Q.	

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[a] All concentrations are reported in mg/L; no entry indicates the compound was not detected.

[b] Not quantified (N.Q.).

[c] Quantified using 3-Methylpentanoic acid standard.

[d] Quantified using 2-Ethylhexanoic acid standard.

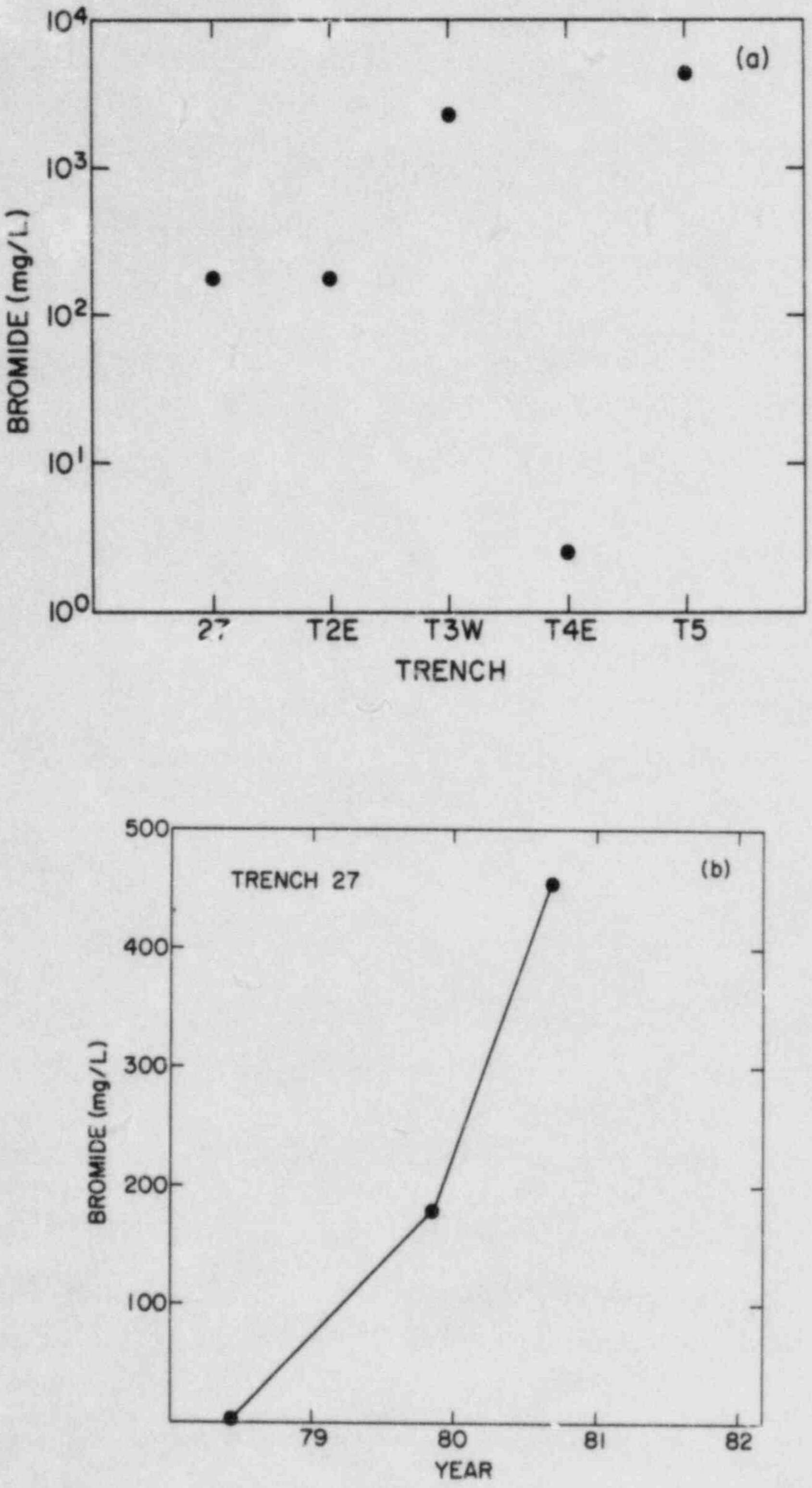

Figure 4.33. Distributions of bromide in waters sampled in the experimental facility area: (a) trench 27 and experimental trench sections; (b) build up of bromide in trench 27 as a function of time.

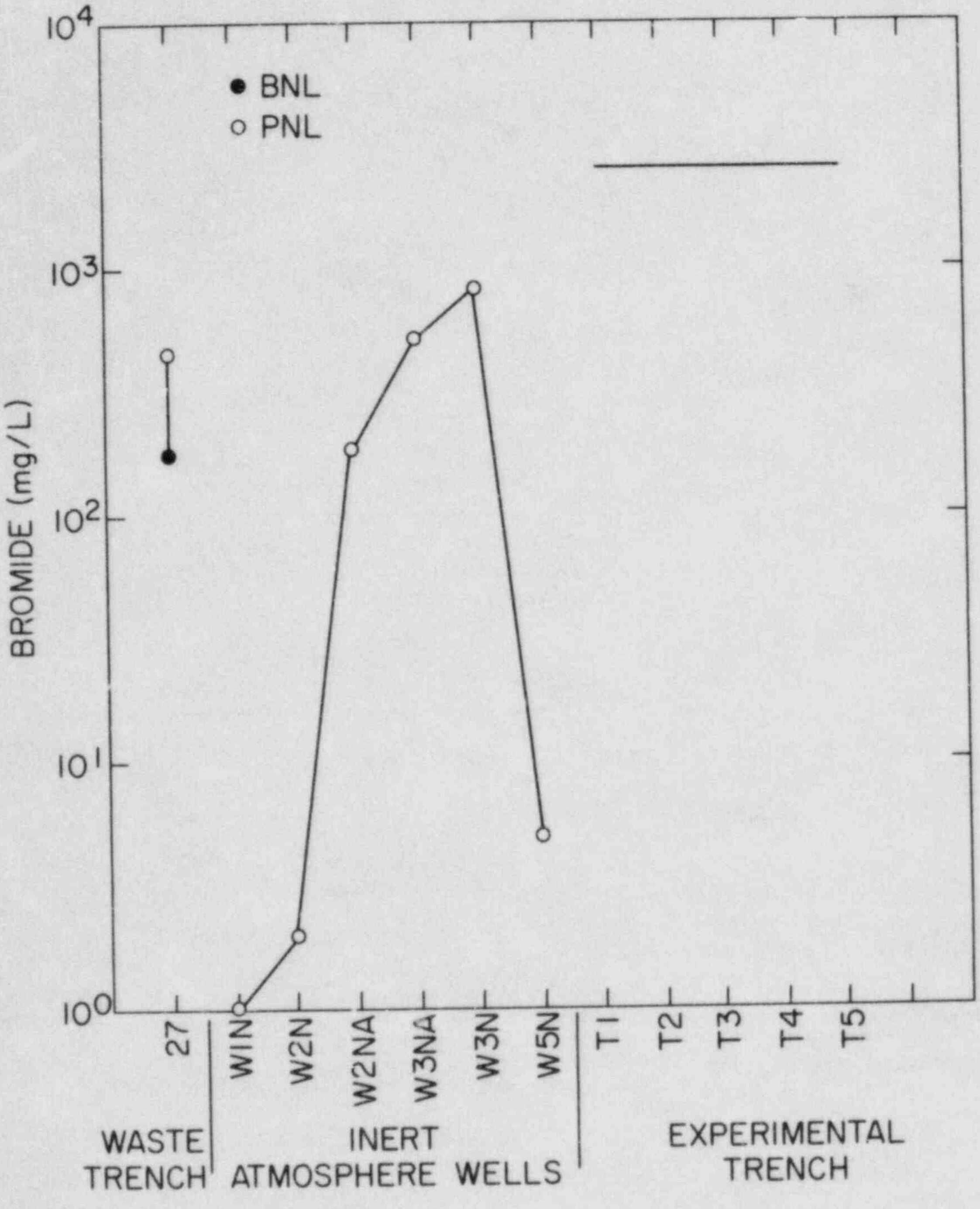

Figure 4.34. Distributions of bromide in waters sampled from trench 27, inert atmosphere wells, and experimental trench sections. The average bromide concentration observed in experimental trench sections T1, T2, T3, and T5 is represented by the solid line. No bromide tracer was added to T4.

Trench 27 and Experimental Trench--Sources of Contaminants

Distributions of other waste derived constituents such as dissolved inorganic carbon, Sr^{2+}, Na^{+}, Ca^{2+}, and alkalinity indicate both waste trench 27 and experimental trench sections to be sources of the contaminants. Apparently crushed limestone was used as backfill material in the experimental trench. Considering that leaching of limestone will release Ca^{2+}, Sr^{2+}, dissolved inorganic carbon and alkalinity, the observed profiles in Figure 4.30 can be attributed to the presence of sources for these contaminants in both the waste trench 27 and the experimental trench sections. The distribution of Na^{+} shown in Figure 4.35 can also be explained in a similar fashion in that Na^{+} was added in the form of NaBr tracer to the experimental trench sections. Depletion of Na^{+} in T4E can be attributed to the fact that no NaBr was added to this particular section of the experimental trench. Furthermore, the profiles in Figure 4.35 show that, irrespective of where the contaminant source is located, the inert wells W2NA and W3NA and experimental trench section T2 exhibit similar and significantly higher concentrations than those observed for the other inert wells and experimental trench sections, indicating excellent communication between waste trench 27, inert wells W2NA and W3NA, and experimental trench section T2 in both directions.

4.2.3.2. Other Observations of in situ Leachate Migration

At the second experimental facility on the disposal site (Figure 1.3), LANL has been involved in studying in situ radionuclide migration in the vicinity of a disposal trench. A series of porous cups were emplaced in the soil near trench 19s to sample interstitial water on a seasonal basis at various depths and at increasing distance from the trench boundary.

The results of the LANL study, as reported by Polzer et al. (1982), show that H-3 was observed as far as ≈35 feet from the trench boundary. Migration of leachate, derived from trench 19s, along a sandstone layer as well as by interstitial flow though the surrounding soil is believed to result in the observed interstitial tritium distributions. The distributions of other radionuclides in soil interstitial waters further indicate that relative to tritium, Pu-238, Co-60, and Cs-137 are less mobile, with the extent of observed migration following the order

$$\text{H-3} > \text{Co-60} \approx \text{Pu-238} > \text{Cs-137}$$

Tritium, chemically bound as HTO, migrates unretarded along with interstitial water in the soil or along the sandstone layer. Cs-137, on the other hand, was not detected in any of the interstitial water samples, indicative of its non-conservative, reactive nature which results in maximum attenuation and lowest mobility. Pu-238 and Co-60 were observed in interstitial waters but not beyond a distance of 7 feet from the trench boundary. Although both Pu-238 and Co-60 are known to exhibit non-conservative geochemical behavior, it is believed, as discussed earlier in this report, that the presence of chelating agents such as EDTA in trench 19s (Table 3.13) can form radionuclide complexes, giving rise to enhanced mobility of Pu-238 and Co-60. Both these radionuclides are known to form relatively stable complexes with EDTA, and the presence of Pu in trenches at Maxey Flats as a Pu-EDTA complex has been reported (Cleveland and Rees, 1981; Kirby et al., 1984). More recently, Polzer et al. (1984) have reported that greater than 95% of the dissolved plutonium in some trench leachates is present as a mobile PuEDTA complex species.

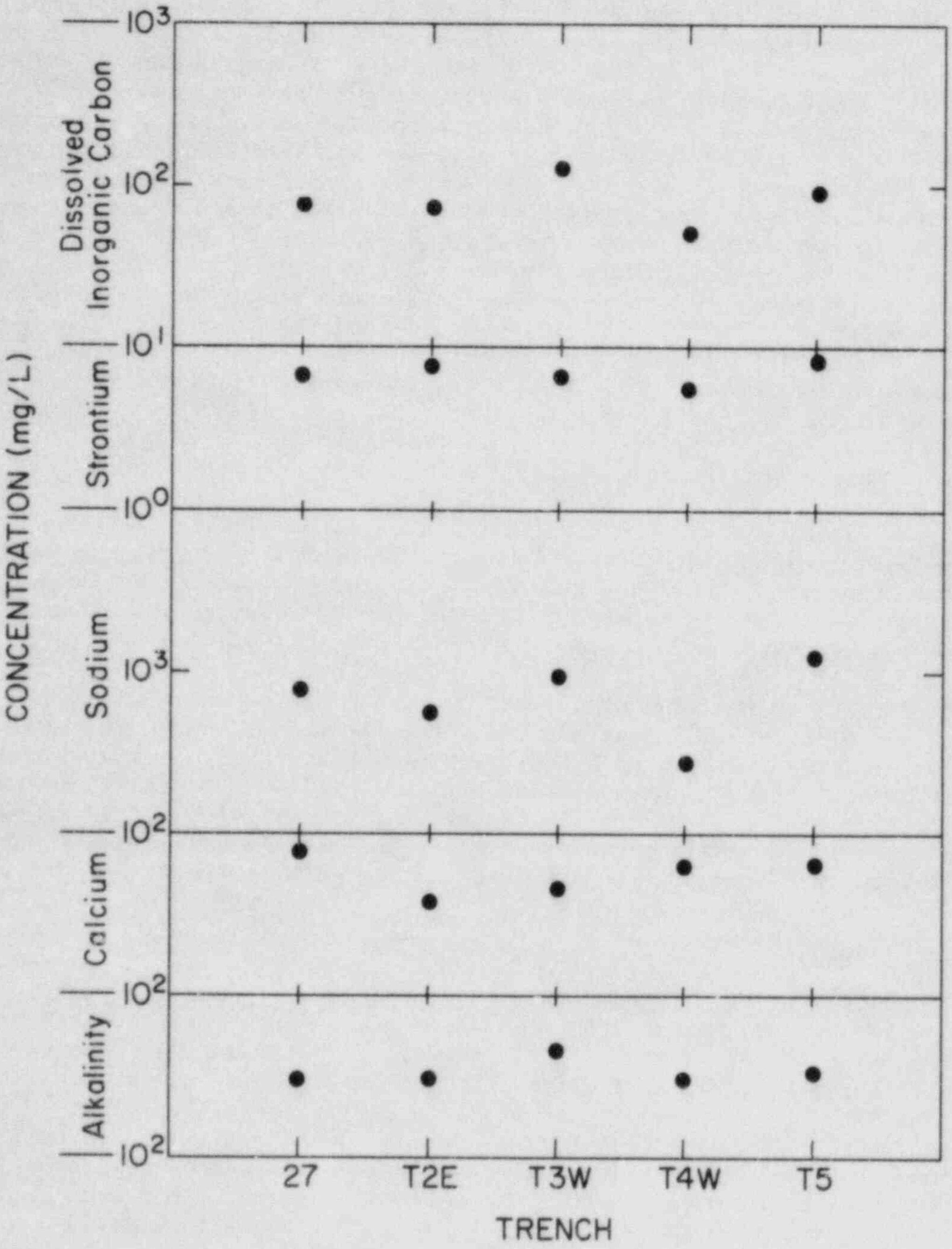

Figure 4.35. Distributions of dissolved inorganic carbon, strontium, sodium, calcium, and alkalinity in waters sampled from trench 27 and experimental trench sections.

On-site wells (UB series) were sampled by BNL repeatedly, along with the trench leachates during the period 1976-1979. Radionuclides and organic contaminants were observed in five wells UB1, UB1A, UB2, UB3, UB4 drilled by USGS, indicating subsurface migration of leachate derived from neighboring trenches. Well water UB1A was found to contain the lowest radionuclide concentrations. Subsequently, well UB1 was grouted to prevent further migration of trench leachates (Weiss and Colombo, 1980). However, well UB1A drilled nearby was left open.

The types and concentration levels of organic and radionuclide contaminants observed in well water UB1 are given in Table 4.15. Subsequent sampling of well water UB1A also showed the presence of organic compounds and radionuclides. Most of the organic compounds present in the well waters are waste-derived and are also observed in the trench leachates. These on-site well observations suggest migration of leachate, presumably derived from neighboring trenches located approximately 35 feet away, by subsurface routes in the general direction of the UB wells. It is believed that transport is through the fractured lower sandstone marker bed which represents the base of most trenches at the site.

In a separate study, Zehner (1983) reported subsurface migration of Co-60 and Mn-54 along the lower sandstone marker bed as much as 270 feet from the nearest burial trench (trench 46). The groundwater velocity is estimated to be 50 ft/yr in the horizonatal direction, based on the rate of travel of the radionuclide front at one location.

Table 4.15. Concentrations of organic compounds and radionuclides observed in well water UB1.[a]

Constituents	Concentration
Organic Compounds	(mg/L)
2-Methylbutyric acid	0.84
2-Methylpentanoic acid[b]	0.73
3-Methylpentanoic acid	0.16
Phenol	0.31
Hexanoic acid	1.1
2-Methylhexanoic acid	0.74
Cresol (isomer)	0.39
Cresol (isomer)	0.38
2-Ethylhexanoic acid	1.6
Benzoic acid	0.40
Octanoic acid	0.38
Phenylacetic acid	0.44
Toluic acid (isomer)	0.13
Toluic acid (isomer)	0.28
Phenylpropionic acid	3.8
Phenylhexanoic acid	N.Q.[c]
p-Dioxane	N.Q.
Toluene	2.7
Xylene	0.12
Naphthalene	0.09
α-Terpineol	0.16
Radionuclides	(pCi/L)
H-3	$4.8\text{x}10^{8}$
Sr-90	$7.1\text{x}10^{4}$
Co-60	$4.7\text{x}10^{3}$
Pu-238	$3.3\text{x}10^{1}$
Pu-239,240	$4.2\text{x}10^{-1}$

[a] Sampling and analysis conducted by BNL (Weiss and Colombo, 1980).

[b] Quantified using 3-Methylpentanoic acid standard.

[c] Not quantified (N.Q.).

5. RELEVANCE OF RESEARCH FINDINGS TO NRC NEEDS

BNL research on the Maxey Flats disposal site has provided some generic insights into such geochemical processes and controls as the mechanics of leachate formation, microbial degradation and development of anoxia, organic complexation and radionuclide mobility, redox inversion and modification in the source term, solubility constraints on solute chemistry, mineral authigenesis, corrosion products and radionuclide scavenging, and the role of organic complexing agents in geochemical partitioning of radionuclides.

A knowledge of such processes and controls affecting the geochemical cycling of radionuclides as well as an understanding of the important factors that contribute to variability and uncertainties in the source term is essential for evaluating the performance of waste package and the site, making valid predictions of release for dose calculations, and for planning site performance monitoring as well as remedial actions.

Based on the observations made at Maxey Flats, it is clear that infiltrated water should not be allowed to accumulate in the trenches, leading to a "Bathtub Effect". Such accumulations of water for extended time periods result in prolonged leaching of waste materials, contributing to elevated concentrations of waste-derived constituents in the trench solutes. Furthermore, because of the long residence time of infiltrated water in the trenches, molecular oxygen is depleted rapidly by aerobic oxidation of organic matter, leading to the development of anoxia in the trenches. Without significant replenishment of accumulated water, the microbial processes continue, leading to a build up of decomposition products which result in strongly anoxic conditions. The development of such redox conditions in the trenches affects the geochemical partitioning of radionuclides, increases their migration potential, and also contributes to uncertainties in the source term, in that drastic changes take place in solute chemistry upon oxidation. Therefore, future shallow land burial sites should be located in well-drained systems where the accumulated water has a short residence time.

Unsegregated, poorly packaged, and unstabilized wastes, which were buried at Maxey Flats, are readily leachable and biodegradable, giving rise to the development of large void spaces and subsequent trench cap subsidence, followed by increased infiltration and accumulation of water in the trenches. This in turn contributes to a greater potential for migration of radionuclides. The presence of complexing agents in unsegregated wastes can also contribute to enhanced nuclide mobility and affect radionuclide partitioning at geochemical interfaces. Because of the extreme heterogeneity of the unsegregated wastes, both in character and composition, the leachate chemistry is highly variable from one trench to another, or even within the same trench.

These problems associated with unsegregated, poorly packaged, and unstabilized wastes lead to the importance of the waste form in providing trench stability, decreasing the rate and extent of leaching and microbial degradation of buried waste, and also reducing the uncertainties in the source term in terms of solute chemistry. In fact, in the trenches where the liquid wastes were solidified with cement (33L4 and 33L8), the solute chemistries were more predictable in terms of low radionuclide concentrations, high Ca^{2+}, Sr^{2+}, and CO_3^{2-} concentrations, high pH, and low concentrations of dissolved organic carbon.

All these problems encountered at the Maxey Flats disposal site point to the need for waste segregation, improved stabilization, and proper packaging to ensure stability. Future sites will most likely be located in well-drained systems, where the residence time of accumulated water is relatively short.

6. SUMMARY AND CONCLUSIONS

- A combination of hydrological and geochemical factors determines to a large extent the formation and compositions of trench leachates. At the Maxey Flats site, the waste trenches are located in non-porous shale of low hydraulic conductivity. This results in accumulations of rainwater that infiltrate through the trench caps. Such accumulation of stagnant water and its eventual overflow, which has been termed the "Bathtub Effect", has been observed in the Maxey Flats trenches.

- Because of the long residence time of accumulated water in the trenches, prolonged leaching and microbial degradation of buried waste material occurs continuously and leads to leachate formation. As a result of such interactions for extended time periods, the resultant trench leachates acquire geochemical properties which are unique, compared to ambient groundwater.

- Relative to ambient groundwater, the Maxey Flats leachates exhibit significant modifications in terms of inorganic, organic, and radionuclide solute constituents, attributable primarily to microbial degradation and leaching of buried waste materials.

- The development of anoxia in trench leachates is largely controlled by microbial degradation of organic matter present in the buried wastes. A large fraction of wastes buried in the trenches consists of unconsolidated organic materials. Many components of these materials are subject to both aerobic and anaerobic microbial degradation processes. The anoxic redox conditions observed in the trench leachates are characterized by negative redox potentials, low dissolved oxygen and sulphate concentrations, the presence of dissolved sulphide, and high contents of alkalinity and ammonia, reflecting the nature and intensity of the microbial processes.

- An evaluation of redox equilibria and redox buffering in trench leachates indicates that Fe_2O_3/Fe^{2+} and SO_4^{2-}/H_2S couples appear to be the dominant buffers controlling the redox conditions in most trench leachates.

- The enrichments, to varying degrees, of inorganic, organic, and radionuclide constituents associated with fuel cycle and non-fuel cycle low-level wastes reflect the nature of the leaching process itself and of the waste materials. Elevated concentrations of Na^+, K^+, Fe_{total}, Mn_{total}, Cl^-, dissolved organic and inorganic carbon and several organic compounds, as well as radionuclides such as H-3, Am-241, Co-60, Cs-134, Cs-137, Sr-90, Pu-238, and Pu-239,240 are a consequence of waste leaching. Some of the waste-derived organic compounds present in the trenches such as chelating agents and several carboxylic acids are strong complexing agents and have the potential to form stable radionuclide complexes and thus enhance nuclide mobility.

- In Maxey Flats trench leachates, representing relatively stagnant systems, where the products of waste leaching and microbial degradation are continually generated and subsequently accumulate, the leachate solutes are also subject to abiogenic precipitation reactions. The WATEQF geochemical code used to calculate saturation states of trench leachates with respect to several mineral phases indicate calcite, dolomite, and rhodochrosite are likely to form and exert control on the concentrations of Ca^{2+}, Mg^{2+}, Mn^{2+}, and CO_3^{2-}. In the case of iron equilibria, gross supersaturations are found with respect to siderite, mackinawite, amorphous FeS and pyrite. Some leachates, however, exhibit saturation with respect to vivianite, indicating that the Fe^{2+} and PO_4^{3-} concentrations are most likely controlled by this mineral phase.

- Laboratory oxidation experiments, performed to obtain generic information on the behavior of anoxic trench leachates as they encounter a less reducing environment along groundwater flow paths, demonstrated that, upon oxidation, a series of chemical changes were initiated which results in a drastically different solute chemistry. The experiments further showed that, even though precipitation of ferric oxyhydroxide occurred in most cases, coprecipitation or scavenging of the radionuclides was minimal. These observations indicate that some of the radionuclides may have formed complexes with organic complexing agents sufficiently stable to withstand scavenging by authigenic ferric oxyhydroxide, which represents a geochemical discontinuity where iron-rich, anoxic waters encounter a more oxidizing environment.

- Evaluation of the balance between the initial alkalinity of trench leachates and the acidity generated as a result of the ferrous iron oxidation reaction shows that the Maxey Flats leachates represent well-buffered systems and that the acid generated is not appreciable to affect the balance between acidity and alkalinity. This is important considering that an acid leachate would not only affect the inorganic and radionuclide solute species but also have a significant effect on leachate-sediment interactions.

- Solubility calculations indicate that, in addition to significant changes observed in solute chemistry upon oxidation, certain carbonate and oxide mineral phases may form and exert control on solute chemistry at geochemical interfaces, representing zones where iron-rich, anoxic waters mix with oxic groundwater. These authigenic minerals could also have an effect on the geochemical partitioning of radionuclides.

- Radionuclide sorption experiments performed to evaluate the role of organic complexing agents in waste migration show that cobalt forms relatively strong complexes with EDTA and NTA and that these complexes persist in strongly reducing, anaerobic environments typical of burial trenches, where anoxic conditions develop. As a result of the formation of such stable complexes, Maxey Flats shale is not very effective in removing cobalt from solution. On the other hand, the sorption of cesium and strontium remains unaffected in the presence of added complexing agents, indicating little affinity for alkali metals towards complex formation. These observations, together with our findings of a lack of removal of radionuclides from solution by authigenic ferric oxyhydroxide in oxidized trench leachates containing complexing agents, indicate the important role organic complexants play in the geochemical partitioning and mobility of radionuclides.

- In situ leachate migration experiments conducted in the vicinity of two burial trenches demonstrated that migration of inorganic, organic, and radionuclide constituents does indeed occur on the disposal site. The experimental trench facility experiments showed that migration of contaminants occurs by subsurface routes both out of and into trench 27. Experiments conducted in the vicinity of trench 19s also indicate subsurface migration of radionuclides away from the trench boundary. Because of its non-reactive nature, tritium was found to be the most mobile, and cesium the least.

- The types and concentrations levels of organic and radionuclide contaminants observed in well waters UB1 and UB1-A also suggest on-site, subsurface migration of leachates, derived from neighboring trenches, in the general direction of the UB wells.

- In most cases, the observed subsurface leachate migration is believed to occur along the fractured lower sandstone marker bed, which represents the base of most trenches at the site.

- Because Na^+, Cl^-, and H-3 are enriched in the trench leachates, as a result of waste leaching, and because they are known to be nonreactive geochemically, they serve as excellent inert tracers for leachate migration, as evident from the observed concentration gradients in the vicinity of trench 27.

- The problems associated with unsegregated, poorly packaged, and unstabilized wastes encountered at the Maxey Flats disposal site point to the need for waste segregation, improved stabilization, and proper packaging. Stabilized, packaged waste not only ensures trench stability but also decreases the rate and extent of leaching and microbial degradation of buried waste. In addition, the uncertainties in the source term are reduced.

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APPENDIX A

CHEMICAL CONSTITUENTS IN FUEL AND NON-FUEL CYCLE WASTES (FROM CLANCY et al., 1983).

Table A-1. Chemical characteristics of fuel and non-fuel cycle low-level waste constituents.

Descriptive Class	Examples	Fuel Cycle	Non-Fuel Cycle
Agricultural compounds	DDT, malathion, [^{14}C, ^{32}P, ^{35}S]		X
Alcohols	methanol, cyclohexanol, diacetone		X
Aldehydes and acetals	paraldehyde, 1, 1,-diethoxyethane		X
Aliphatic halogenated hydrocarbons	1,1,1-trichloroethane		X
Alkanes	cyclohexane		X
Alkenes	2,3-dimethyl-2-hexene		X
Alkyl halides	1-isobutyl-4-ethyloctyl bromide		
Amino acids	alanine, tryptohan [^{3}H, ^{14}C, ^{35}S]		X
Amino sugars			X
Ammonia and ammonium salts	ammonia, ammonium sulfate	X	
Aromatic hydrocarbons	benzene, toluene, p-xylene anthracenes, dibenzene anthracene [^{14}C]		X
Asphalt	natural or petroleum-derived	X	
Carboxylic acids	citric acid, tartaric acid oxalic acid, hydroxy-acetic acid	X	X
Chelating agents	EDTA	X	X
	DTPA	X	X
	NTA		
	TTHA	X	X
Carbohydrates	2-deoxy-d-glucose, [^{3}H, ^{14}C]		X
Drugs	acetylsalicyclic acid, actinomycin D, [^{14}C, ^{35}S]		X

Table A-1. Chemical characteristics of fuel and non-fuel cycle low-level waste constituents. (continued)

Descriptive Class	Examples	Fuel Cycle	Non-Fuel Cycle
Esters			
Acetates	ethyl acetate		X
Adipates	dioctyl adipate, bis-2-ethylhexyl adipate		X
Biocarbons	natural or metabolic products of organisms		X
Borates	sodium teraborate, metaborate boric acid, borate polymers	X	
Heptonates	stannous glucoheptonate		X
Phosphates	chromic phosphate, tributyl phosphate, sodium phosphate stannous polyphosphate, orthophosphates, ^{32}P		X
Phthalates	di-2-ethylhexyl, diethyl dibutyl, dioctyl phthalates	X	X
Sulfates	ammonium sulfates, calcium sulfate, sodium sulfate, other sulfate salts, ^{35}S	X	X
Ethers	bis(2-chloroethyl) ether, tetrahydrofuran 1,4-dioxane		X
Fatty acids	linoleic acid, oleic acid, oxalic acid, palmitic acid, $[^{3}H, ^{14}C]$		X
Hormones	histimine dihydrochloride		X
Inorganic acids	boric acid, phosphoric acid, sulfuric acid, $[^{32}P]$	X	X
Ketones	methyl isobutyl ketone, d-fenchone		X

Table A-1. Chemical characteristics of fuel and non-fuel cycle low-level waste constituents (continued).

Descriptive Class	Examples	Fuel Cycle	Non-Fuel Cycle
Lipid-related products	actylocholine chloride, sphingomyeline [^{3}H, ^{14}C]		X
Miscellaneous inorganic	calcium fluoride, chloride, copper, diatomaceous earth, fluoride, portlane cement, Mg, Zn, sodium hydroxide, sodium iodide	X	X
Nitrosamines	N,N-dimethylnitrosamine		X
Nucleosides	---		X
Nucleotides	adenosine-3',5'-cyclic phosphate [^{3}H, ^{14}C, ^{32}P, ^{125}I]		X
Nucleotide sugars	guanosine diphospho-1-fucose, [^{14}C]		X
Organic acids	acetic acid, benzoic acid, iodoacetic acid, phenylhexanoic acid		X
Peptides	---		X
Phenol and phenolic compounds	cresols, p-tert-butyl phenol		X
Prostaglandins [^{3}H, ^{19}C]	Prostaglandin E_2		X
Proteins	---		X
Protein-labelling reagents	acetic amhydride, 1-fluoro-2,4-dinitrobenzene, phenylisothiocycanate, [^{3}H, ^{14}C, ^{32}P, ^{35}S, ^{125}I, ^{131}I]		X

Table A-1. Chemical characteristics of fuel and non-fuel cycle low-level waste constituents. (continued)

Descriptive Class	Examples	Fuel Cycle	Non-Fuel Cycle
Purines	adenine, guanine sulfate [^{3}H, ^{14}C]		X
Pyrimidines	uracil [^{3}H, ^{14}C]		X
Radionuclides	Ba-137m, 139, 140	X	
	C-14		X
	Cs-144	X	
	Co-58, 60	X	
	Cs-134, 136, 137, 138	X	
	Cr-51	X	
	H-3		X
	I-125, 131		X
	I-129	X	
	I-130, 132, 133, 134, 135	X	
	Fe-55, 59	X	
	La-140	X	
	Mn-54	X	
	Mo-99	X	
	Na-22		X
	P-32		X
	Pu	X	
	Rb-88		X
	Sr-89, 90, 91, 92	X	
	S-35		X
	Tc-99		X
	Th	X	
	U-naturals and daughters	X	
	Y-90, 91	X	
	Zr-95	X	
Resins	ion-exchange, urea formaldehyde	X	X
SterIods	aldosterone, estradiol, progesterene		X X
Vitamins	nicotinamide		X

Table A-2. Summary of chemical constituents in fuel cycle low-level wastes.

Organic Compounds

asphalt (solidification agents)
urea-formaldehyde resins
  (may contain alkali metal
  bisulfates)
carboxylic acids (decontaminating
  chemicals)
chelating agents
  (NTA, EDTA, DTPA, TTHA)

ion exchange resins
  (sulfonated and aminated organic
  polymers; modified plystrenes,
  copolymers of divinyl benzene
  and styrene are typical substrates)
phthalates
  (for filter testing)
vinyl ester styrene

Inorganic Compounds

ammonia
ammonium sulfate
boric acid
calcium fluoride
calcium sulfate
sodium tetraborate, metaborate
portland cement
  (with or without bentonite or
  vermiculite)
diatomaceous earth

Elemental Species

barium-137m, 139, 140
bromine-84
cerium-144
cesium-134, 136, 137, 138
chloride (Cl)
chromium-51
  oxide or hydrated oxide
cobalt-58,60
  oxide or hydrated oxide
copper
fluoride
F^-, metallic fluorides
iodine-129, 131, 132, 133, 134, 135
iron-55, 59
  oxide or hydrated oxide
lanthanum-140
magnesium
manganese-54
  oxide or hydrated oxide
molybdenum-99
niobium-95
Pu
rubidium-103, 106
strontium-89, 90, 91, 92
uranium
  natural U and daughters
Tellurium-132, 134
Th
Tritium
Yttrium-90, 91
zinc
zirconium-95
  oxide or hydrated oxide

Table A-3. Summary of identifiable chemicals in non-fuel cycle wastes.

Scintillation Vials	Other Liquids	Solid Waste	Biological Waste
toluene, xylene, sodium hydroxide; (with small amounts of methanol); aquasols, POP	50% is spent scintillation fluids. Other liquids are ogranic waste, alcohol, benzene, ethyl acetate, and RIA Kits which may contain any of the following compounds: ammonium sulfate, sodium barbital, sodium azide, ammonium salt, sulfonic acids, colloids, stannous polyphosphate, stannous glucoheptonate, amino sugars, amino acids, nucleosides, nucleotides, protein hydrolysates, pyruvic acid, $NaHCO_3$, anthracene compounds, phosphoric acid, iodoacetic acid, Bolton-Hunter reagent, iododeoxyuridine, sodium iodide, organic phosphates, orthophosphates, methionine, tritiated thymodine, ethidium bromide (intercalating dye), paradimethyl amino benzalide (PDAB), ethylenediaminetetraacetic acid (EDTA) additional possible liquid waste could be solutions of any of the labeled compounds found in Appendix A-1	cellulosics, PVC plastics, rubber, glass, metal filings, other trash.	animal carcasses, cultures disinfected with Clorox^R, Beau Coup^R (a phenol solution), or Wescodyn^R (iodine base); or contaminated animal wastes.

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As part of the NRC efforts to develop a data base on source term characteristics for low level wastes, Brookhaven National Laboratory (BNL) has produced and analyzed a large amount of data on trench leachate chemistry at existing shallow land burial sites. In this report, we present the results of our investigations at the Maxey Flats, Kentucky disposal site. In particular, data on trench leachate chemistry are reviewed and discussed in terms of mechanisms and processes controlling the composition of trench solutes. Particular emphasis is placed on identifying both intra- and extra-trench factors and processes contributing to source term characteristics, modifications, and uncertainties. The problems associated with unsegregated, poorly packaged, and unstabilized wastes encountered at the Maxey Flats disposal site point to the need for waste segregation, improved stabilization, and proper packaging. Stabilized, packaged waste not only ensures trench stability but also decreases the rate and extent of leaching and microbial degradation of buried waste. In addition, the uncertainties in the source term are reduced.

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