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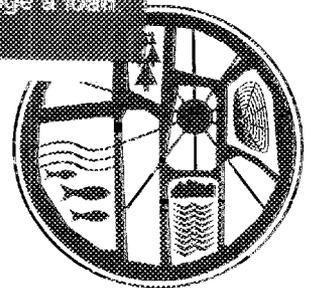
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**Groundwater Monitoring in 1988 at
Three Oak Ridge National Laboratory
Inactive Waste Impoundments**

D. K. Solomon
D. S. Wickliff
O. M. Sealand
C. W. Francis

Environmental Sciences Division
Publication No. 3235

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ENVIRONMENTAL SCIENCES DIVISION
GROUNDWATER MONITORING IN 1988 AT THREE OAK RIDGE NATIONAL LABORATORY
INACTIVE WASTE IMPOUNDMENTS

D. K. Solomon, D. S. Wickliff, O. M. Sealand, and C. W. Francis

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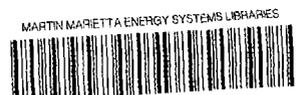
NUCLEAR AND CHEMICAL WASTE PROGRAMS
(Activity Nos. AH 10 20 00 0 and GF 11 04 00 0)

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ABSTRACT

SOLOMON, D. K., D. S. WICKLIFF, O. M. SEALAND, and C. W. FRANCIS. 1989. Groundwater monitoring in 1988 at three Oak Ridge National Laboratory inactive waste impoundments. ORNL/TM-11022. Oak Ridge National Laboratory, Oak Ridge, Tennessee. 79 pp.

Three unlined impoundments were formerly used to collect and, in some instances, treat wastewater generated at Oak Ridge National Laboratory (ORNL). They are (1) the 3513 Waste Holding Basin, (2) the Old Hydrofracture Facility (OHF) impoundment, and (3) the Homogeneous Reactor Experiment No. 2 (HRE) impoundment. To determine if the migration of contaminants from these impoundments presents a threat to groundwater quality, at least one upgradient groundwater monitoring well and three downgradient monitoring wells were installed in 1985. Groundwater monitoring during 1986 and 1987 revealed that the principal contaminants found in groundwater downgradient from the impoundments were radionuclides, namely ^{90}Sr and tritium. Previous groundwater monitoring was focused largely on analyses of groundwater for toxic metals (Ag, As, Ba, Cd, Cr, Hg, Pb, Se), other constituents contained in EPA's primary drinking water standards, and radionuclides. Other than the analyses for total organic carbon and total organic halides, little attention was given to the detection of hazardous organic compounds in groundwater. The major objective in the 1988 sampling at these impoundments was to determine if hazardous organic compounds, namely volatile and semivolatile organics, are leaching into groundwater from these impoundments.

Detectable levels of organic compounds were measured in groundwater at all three impoundments. Relatively large concentrations of carbon tetrachloride and chloroform (22 to 214 $\mu\text{g}/\text{L}$ and 17 to 77 $\mu\text{g}/\text{L}$, respectively) were measured in groundwater sampled from all monitoring wells at the OHF site. Mean concentrations of carbon tetrachloride and chloroform in water taken from the OHF downgradient wells were not statistically different from the concentrations measured in the upgradient well, indicating that the source of the compounds leaking into groundwater is likely wastes buried in a low-level radioactive waste burial ground located upgradient from the OHF impoundment. Trichloroethene as well as 1,1-di-chloroethane and 1,1,1-trichloroethane were also detected in the upgradient and downgradient groundwater at the OHF site. Concentrations of 1,2-dichloroethane (contained in machining solvents and degreasers) were observed in groundwater sampled from both the downgradient as well as the upgradient wells at 3513, indicating likely contamination from a source upgradient from the impoundment.

In general, organic compounds were detected in water sampled from wells upgradient and wells downgradient from the impoundment site indicating that the impoundments are not sources of organic compounds leaching into groundwater.

1. INTRODUCTION

In response to regulations promulgated under the Resource Conservation and Recovery Act (RCRA), Oak Ridge National Laboratory (ORNL) has established a groundwater monitoring program to evaluate groundwater quality. One of the sources to groundwater contamination on the ORNL reservation is contaminants contained in waste holding basins used to collect and dispose of low-activity low-level liquid waste streams. These basins or impoundments (also called waste ponds) are unlined, and in many cases the sediment or precipitated floc present at the bottom of the impoundment is in direct contact with the nearby groundwater. Groundwater monitoring wells were installed at three inactive waste impoundments in the spring of 1985. These included the 3513 impoundment within the main plant area, the Old Hydrofracture Facility impoundment (OHF), and an earth-filled impoundment covered with an asphaltic cap at the Homogeneous Reactor Experiment (HRE) site. Details of the construction and location of these monitoring wells have been documented in other reports (Stansfield and Francis 1986a, 1986b, and 1986c). A report (Francis and Stansfield 1986) evaluating the groundwater monitoring data after 1 year of data collection (four quarters) revealed that the principal contaminants found in groundwater downgradient from the impoundments were radionuclides, namely ^{90}Sr and tritium.

At the OHF site the mean level of tritium measured in the upgradient well (about 91,000 Bq/L as compared with 80,000 Bq/L in the downgradient wells) indicated that the groundwater had been affected by wastes buried in the low-level radioactive solid waste storage area (SWSA-5) upgradient from the impoundment. One monitoring well (no.4) downgradient from the OHF site showed high concentrations of ^{90}Sr in groundwater (~ 1200 Bq/L) as compared to <2 Bq/L in the groundwater upgradient of the impoundment. A ^{85}Sr tracer study at this site revealed that ^{85}Sr added to the pond water was detected in groundwater at ~ 50 d and a peak in ^{85}Sr concentration was seen in about 100 d (C. W. Francis, personal

communication, July 1988). The observed transport velocity of ^{85}Sr was calculated to be on the order of 0.15 ft/d. By using a retardation factor of 35 for ^{85}Sr [cited by Spalding and Munro (1984) for a similar soil], values of 5.4 ft/d and 0.018 for seepage velocity and effective porosity, respectively, were determined, confirming that movement of ^{90}Sr from the OHF impoundment is not simple seepage through porous media, but rather leakage in the form of flow along fractures in the underlying rock.

At the 3513 impoundment the groundwater monitoring from February 1985 to January 1986 had indicated that the downgradient groundwater had been contaminated by chromium and lead and possibly halogenated organic compounds. For example, the mean concentrations of these metals in groundwater from monitoring wells downgradient from the impoundment were 0.15 and 0.18 mg/L, respectively for lead and chromium as compared with RCRA limits of 0.05 mg/L. The gross beta limit for the primary drinking water standard (4 mR/year, assuming a person drinks 2.2 L of water per day for a year) was exceeded at the 3513 site by either ^{90}Sr or tritium levels in groundwater downgradient from the impoundment.

At the HRE site two groundwater samples taken in 1985 contained herbicides slightly in excess of the RCRA limit. This was the first and only instance of herbicide detection in groundwater at any of the three impoundments. Sodium borate was used to kill weeds during backfilling of the HRE impoundment; however, there is no record of the use of Endrin or Toxaphene.

At all three sites during the first year of groundwater monitoring, levels of fecal coliform bacteria, in excess of the RCRA limit were often observed. This was the case regardless of where the water sample was taken, from monitoring wells upgradient or downgradient from the impoundments.

Groundwater from monitoring wells at all three impoundments was again sampled in the first and second quarters of 1987 (C. W. Francis, personal communication, September 1987). The principal objective in this sampling was to verify, or refute, the contamination of groundwater at these sites

by some of the toxic metals, namely the presence of excessive levels of lead and chromium in groundwater downgradient from the 3513 site. Also of interest, were the levels of fecal coliform bacteria in groundwater at these sites. The 1987 data generally refuted any evidence that the leaching of heavy metals such as Pb, Cr, or Ba is occurring at levels in excess of the RCRA limit. Also, there was no evidence of fecal coliform bacteria in groundwater sampled in 1987, indicating that the measurements of fecal coliform bacteria during the 1985 sampling were likely an artifact in sampling and/or analyses. It was also suggested that future monitoring at these sites be limited to an annual basis but should be expanded to include all RCRA primary drinking water constituents [as defined in 40CFR Part 264.94 (a) (2)] as well as those radionuclides detected during the 1985 and 1987 monitoring.

Groundwater sampling in 1988 was significantly more comprehensive with respect to quality control in sampling and emphasized the detection of specific organic compounds to a greater extent than did the previous groundwater sampling at these impoundments. One of the major objectives in the 1988 sampling was to determine if hazardous organic compounds, namely volatile and semivolatile organics, are leaching into groundwater from these impoundments.

2. METHODS AND MATERIALS

2.1 INSTALLATION OF DEDICATED SAMPLING PUMPS

Dedicated positive displacement (bladder) sampling pumps were installed in four wells at the OHF site in May of 1987 (O. M. Sealand, personal communication, June 1987). The pumps were new, and a dilute solution of HCl was pumped through the pump chamber and tubing prior to installation. Similar pumps were installed at the 3513 and HRE sites in June and July of 1988. The location and description of the monitoring wells at each of the sites, as well as the placement of the sampling pumps in each of the wells, are described in Tables 1 and 2. Groundwater was sampled from July 29, 1988, through August 8, 1988.

2.2 FIELD MEASUREMENTS METHODS

A Surveyor II water quality meter was used to measure specific conductance, pH, dissolved oxygen (DO), and oxidation-reduction potential (ORP). This unit, manufactured by the Hydrolab Corporation, Austin, Texas, is a portable self-contained instrument powered by a rechargeable battery pack. The unit was calibrated according to manufacture's recommended procedures prior to use (normally in the morning before sampling) and again after groundwater measurements. All calibrations were recorded in a registered technical notebook (A-103095-G).

The following sequence of procedures was used in the collection of groundwater samples from each of the monitoring wells at the 3513, HRE, and OHF sites.

1. Calibrate the Surveyor II water quality meter.
2. Measure the static water level by using the standard operational procedure outlined in the Appendix.

3. Determine the volume of water in the monitoring well and purge the well by following the procedures described in the Appendix.
4. Collect the groundwater samples, following the procedures described in the Appendix.
5. Maintain custody of samples and complete all field log sheets, chain-of-custody forms, and sample labels following the procedures described in the Appendix.
6. Complete request for Analytical Services Form and submit samples to the appropriate laboratory in the Analytical Chemistry Division, ORNL, using the procedures established in the Appendix.

Field measurements included four determinations of pH, specific conductance, temperature, DO, and ORP using the Surveyor II water quality meter linked to a flow-thorough cell during collection of the sample for laboratory analysis (e.g., anions, metals, organics and radionuclides). Prior to collection of the groundwater samples each of the wells was purged (step 3 above). Similar field measurements were also recorded during the purging of the well to alert the investigators of any changes that might be taking place.

2.3 SAMPLE PRESERVATION, HANDLING, DOCUMENTATION, AND CHAIN OF CUSTODY

The type of container used to collect the sample, the volume of sample, and the method of sample preservation are outlined in Table 3. These steps are further described in the standard operating procedures (Appendix). Sample containers were purchased precleaned according to the U.S. Environmental Protection Agency's (EPA's) specifications from I-Chem, Inc. Sample collection has been documented in technical notebook No. A-103095-G. Completed field log sheets conforming to those described in the standard operating procedures (Appendix) are pasted in this notebook in the order of sample collection. Well identification labels were used in the field as well as on the Request for Analytical Services form so that the samples could be readily identified. One of

Table 1. Location and description of monitoring wells

Site	Well no.	ORNL Coordinates (m)		Casing diameter (cm)	Type*
		North	East		
3513	1	6542.0	9496.8	5.1	U
	1A	6541.7	9496.1	5.1	U
	2	6455.8	9491.9	5.1	D
	3	6455.8	9451.6	5.1	D
	4	6486.7	9439.7	5.1	D
HRE	1	5679.9	9577.7	7.6	U
	2	5663.6	9611.4	7.6	D
	3	5644.5	9609.1	7.6	D
	4	5643.5	9584.3	7.6	D
OHF	1	5280.7	8717.4	7.6	U
	2	5253.5	8688.3	7.6	D
	3	5272.7	8685.8	7.6	D
	4	5285.0	8692.6	7.6	D

*U = upgradient and D = downgradient from the impoundment.

Table 2. Placement of dedicated sampling pumps

Site	Well no.	Depth to top of screen* (m)	Depth to bottom of screen* (m)	Depth to pump intake* (m)
3513	1	1.76	3.92	2.83
	1A	4.36	7.40	6.94
	2	2.07	5.08	4.75
	3	1.86	4.91	4.58
	4	2.01	4.92	4.59
HRE	1	4.94	9.04	8.58
	2	3.87	7.58	7.12
	3	3.75	6.53	6.07
	4	2.65	6.64	6.18
OHF	1	5.85	8.90	8.59
	2	3.75	6.80	6.49
	3	3.11	6.16	5.85
	4	3.08	6.13	5.82

*Measured from the top of the well casing.

the following suffixes was attached to each sample ID to designate the type of analytical procedure applicable: VO (volatile organics), SVO (semivolatile organics), TM (total metals), DM (dissolved metals), RAD (radionuclides), and AN (anions). A chain-of-custody procedure described in the Appendix was used for all samples.

2.4 ASSESSMENT OF ACCURACY AND PRECISION IN ANALYSES OF GROUNDWATER

Blank groundwater samples were submitted for analytical analysis. Samples of ASTM Type II water were passed through groundwater sampling equipment to assess potential "cross-contamination." These blanks were prepared at the impoundment sites as part of the groundwater sampling protocol. Blank samples were submitted to the Analytical Chemistry Division for the analysis of organics (volatile and semivolatile), anions, metals (dissolved and total), and radionuclides.

Although exact requirements for duplicates are not included under RCRA protocol, duplication of about 10% of the total number of analyses per project has typically been used. To estimate precision in collection of groundwater samples combined with the associated analytical error, duplicate groundwater samples were submitted from 1 of the 13 monitoring wells (no. 3 well at the 3513 impoundment). Requested analysis included metals (dissolved and total), anions, organics (total and semivolatile), and radionuclides. The duplicate sample was collected immediately following the collection of the first. The purging and field measurements were not repeated.

To assess accuracy, metals and radionuclides were added to ASTM Type II water and submitted for analyses. Preservation and type of containers were the same as those used in the sampling of groundwater. Only standards of metals (obtained from the National Bureau of Standards) and radionuclides (obtained from EPA, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada) were used in this study.

Table 3. Sample collection, containerization, and preservatives

Sequence	Parameter	Container type	Volume required (mL)	Number of aliquots	Preservatives	Holding time	Comments
1	Field measurements	NA	NA	NA	NA	NA	Record in field
2	Volatile organics	Amber glass with Teflon septa	40	1	4°C	7 d	Pump rate <100 mL/min*
3	Semivolatile organics	Amber glass	1000	1	4°C	7 d	
4	Field measurements	NA	NA	NA	NA	NA	Record in field
5	Total metals	HDP	500	1	pH <2	6 months	Wrap in foil
6	Dissolved metals	HDP	500	1	Filter 0.45µm pH <2	6 months	Wrap in foil
7	Anions	HDP	500	1	Filter 0.45µm 4°C	28 d	
8	Field measurements	NA	NA	NA	NA	NA	Record in field
9	Tritium	HDP	250	1	Filter 0.45µm	6 months	
10	Other radionuclides ^b	HDP	1000	2	Filter 0.45µm	6 months	
11	Alkalinity	NA	NA	NA	NA	NA	NA
12	Field measurements	NA	NA	NA	NA	NA	Record in field
13	Alkalinity	NA	NA	NA	NA	NA	NA

NA = not applicable; HDP = high-density polyethylene.

*The flow rate should be as low as possible, but sufficient to fill the vial in one pulse of the bladder pump.

^bGross alpha and beta radioactivity, gamma emitters, and ¹⁴C.

2.5 ANALYSIS OF SAMPLES

Analysis of groundwater samples was performed by the Analytical Chemistry Division. Analytes included (1) constituents that were previously detected at levels that were consistently above the proposed RCRA limit, (2) constituents which might be present but were not included in previous analysis, and (3) parameters to characterize the major ion chemistry of the water.

2.5.1 Indicator Parameters

Title 40, CFR (Subpart F, Groundwater Protection, paragraph 265.92) requires that each of the indicator parameters [pH, specific conductance, total organic carbon (TOC) and total organic halogens (TOX)] for every sample taken from a monitoring well be compared with background levels in the upgradient wells averaged over the first four quarters of groundwater monitoring. This requirement was fulfilled by Francis and Stansfield (1986). To evaluate general groundwater quality, specific conductance, pH, DO, and ORP were measured in the field (see previous discussion). TOC and TOX were not measured since an analysis of organic compounds (volatile and semivolatile) was carried out.

2.5.2 Radionuclides

Gamma-emitting radionuclides were measured using gamma spectroscopy. Explicit detection limits were specified for ^{60}Co (1 Bq/L) and ^{137}Cs (1 Bq/L). Scans for other gamma-emitting radionuclides were conducted. A gross beta analysis was performed with a specified detection limit of 0.3 Bq/L. Individual analysis for the following beta-emitting radionuclides was also conducted: ^3H , ^{14}C , ^{99}Tc , and ^{90}Sr . Technetium-99 is a weak beta emitter and would not be adequately detected by the gross beta analysis. Carbon-14, although not considered to be a weak beta emitter, would not be detected in acidified groundwater samples by the method used to determine gross beta activity. The same would hold true

for any ^3H activity in the groundwater samples. Strontium-90 has been previously measured at levels significantly greater than the proposed RCRA limit. Detection limits were specified for ^3H , 500 Bq/L; ^{14}C , 50 Bq/L; ^{99}Tc , 100 Bq/L; ^{90}Sr , 1 Bq/L. These limits are significantly lower than the proposed RCRA limit for each radionuclide and should be sufficient to allow a cumulative risk assessment, based on the existence of multiple contaminants, to be performed. These detection limits represent limits that can reasonably be obtained by using standard methods.

A gross alpha analysis was performed on each sample with a specified detection limit of 0.56 Bq/L. Analysis for individual alpha-emitting radionuclides would have been performed on each sample if the gross alpha activity for that sample was found to be greater than 2 Bq/L. None of the groundwater samples analyzed showed gross alpha activity in excess of 2 Bq/L. Radium-226 was measured during 1985 and was below the RCRA limit or the analytical detection limit in all but one well. Three subsequent analyses from the offending well were all below the detection limit and thus ^{226}Ra was not routinely measured; however, ^{226}Ra analyses would have been performed on all samples having a gross alpha activity greater than 2 Bq/L so that an accounting of gross alpha activity could have been made.

2.5.3 Metals

Metals were measured using inductively coupled plasma spectroscopy (ICP), using EPA method 200.7 (EPA 1986). The ICP method is inexpensive and yields analysis for about 30 elements in a single run. The detection limit of the ICP is below the proposed RCRA toxicity limits (51 FR 21648-21693) with the following exceptions: Hg, Se, Tl, As, Cd, and Pb. Mercury and selenium were measured 4 times in 1985 using special atomic absorption (AA) techniques and were always significantly lower than the proposed limit. Thus special AA techniques for mercury and selenium were not used. Thallium has not previously been measured and requires a very specialized technique to obtain the proposed RCRA limit. Since the

concentrations of all other hazardous metals have been below, or only slightly above, the proposed RCRA limit, special analytical techniques for thallium could not be justified. The concentrations of arsenic and cadmium were at or below the National Pollutant Discharge Elimination System (NPDES) limit in all wells during the four samplings in 1985. Lead was above the NPDES limit in several wells during 1985; however, lead was below the limit in all wells during 1987. The detection limit of the ICP method for many of the above metals will not allow the calculation of a cumulative risk assessment. However, previous groundwater analyses at these sites were completed using more precise methods, i.e., AA techniques. Thus these earlier measurements will be used as baseline values for these metals, and the added expense of more specialized analytical procedures than ICP for metals was not considered to be warranted.

2.5.4 Anions

Anions (NO_3 , F, SO_4 , Cl, Br, PO_4) were measured by using ion chromatography with a conductivity detector (EPA method 300.0, EPA 1983). Alkalinity was determined in the field by titration with 0.01 N HCl. Chloride and nitrate are useful indicators of contamination. The anions F, SO_4 , Cl, Br, and PO_4 as well as alkalinity, were measured to describe ion chemistry of the groundwater. Although the ion chromatographic method for NO_3 is very precise, it has not yet been approved by EPA for NPDES-level analyses. A separate NO_3 analysis using an approved method [e.g., EPA method 353.3 (cadmium reduction)], however was not utilized since significant concentrations of NO_3 were not previously measured in any of the wells. Similar results were obtained in this sampling.

2.5.5 Volatile and Semivolatile Organic Compounds

Gas chromatographic, mass spectrometric (GCMS) techniques were used to analyze for volatile and semivolatile organic compounds (EPA methods 624 and 625, respectively). Previous groundwater monitoring at the impoundment sites was limited to TOC and TOX analyses based on the guidelines established in Title 40, CFR (Subpart F, Groundwater Protection, paragraph 265.92). The TOC and TOX analyses indicated the presence of organic compounds, and thus it is necessary to include volatile and semivolatile organics as analytes to determine if any hazardous organic chemicals are leaching from these impoundments.

The use of GCMS procedures allows for analyses of a wide range of volatile and semivolatile organic compounds, usually on the order of 60 individual compounds. Reporting of results from such analyses produces voluminous tables. In many instances concentrations of organic compounds are below analytical detection levels; thus the tables often form a list of detection limits. In certain cases organic compounds are detected; however, the detectable level is below a standardized quantitative range established for a particular procedure (using reference samples and calibration curves, etc.). Thus, the compound might be detected in a specific sample, but its level cannot be reported with assurance. In this instance the detected value is only an estimate. For this report, only values detected within the established quantitative range are reported.

2.5.6 Pesticides and Polychlorinated Biphenyls (PCBs)

Although pesticides and PCBs were detected in two wells (both at the HRE pond) in 1985, the concentrations were only slightly above or at the proposed RCRA limit. Analyses for pesticides were also conducted in 1987, and pesticides were not detected in any of the samples. For these reasons, these analytes were not included in the 1988 sampling and analyses program.

3. RESULTS AND DISCUSSION

3.1 FIELD MEASUREMENTS

The water levels, pH, DO concentrations, specific conductance, oxygen reduction potential (ORP), and alkalinity (Table 4) were determined at the well site following well evacuation (Table 5). Sample collection and well evacuation summary sheets as well as the alkalinity titration data are contained in the ORNL technical notebook No. A-103095-G. Also contained in this technical notebook are calibration measurements for the Hydrolab Corporation Model Surveyor II monitoring instrument before and after field measurements in addition to any field observations or measurements made during the sampling of the impoundment groundwater monitoring wells. The notebook also contains the information used to install the dedicated positive displacement pumps (Well Wizard Model T-1200) at the 3513 and HRE sites.

Field measurements indicate that the characteristics of the groundwater did not vary greatly from one impoundment site to another. The single exception is groundwater from the no. 4 monitoring well at the OHF site. Water from this well is considerably more acid (pH of ~ 5.5 as compared with ~ 6.1 to 6.8) and displays a much lower specific conductance reading (~ 80 $\mu\text{S}/\text{cm}$) versus the 200-300 $\mu\text{S}/\text{cm}$ in the water from other sites. This is the well in which ^{85}Sr added to the OHF impoundment water was detected after approximately 50 d. Concentrations of ^{90}Sr in groundwater from this well (an average concentration of ~ 1100 Bq/L over a 3-year interval) were relatively high compared to those in groundwater measured in other wells downgradient from the OHF impoundment (<75 Bq/L) and were approximately one-third the concentration of ^{90}Sr in the impoundment water (3900 Bq/L), indicating a close linkage between this well and impoundment water (C. W. Francis, personal communication, July 1988).

Table 4. Field measurements at the 3513, Homogeneous Reactor Experiment, and Old Hydrofracture Facility monitoring wells

Site	Well	Sample date	Water elevation (m)	pH ^a	Dissolved ^a oxygen (ng/L)	Electrical conductivity* (μ S/cm)	ORP ^a (V)	Alkalinity ^b (meq/L)
3513	1A	07/29/88	237.4	6.66	0.37	215	-0.093	6.6
	1	08/02/88	237.5	6.24 ^c	0.39	325	-0.010	8.3
	2	08/03/88	236.5	6.73 ^c	0.35	669	-0.036	5.8
	3	08/03/88	235.5	6.64	0.82 ^d	225	-0.098	6.7
	4	08/03/88	236.0	6.32	0.27	267	-0.049	8.2
HRE	1	08/04/88	248.1	6.79	1.55	194 ^c	-0.047	4.4
	2	08/05/88	246.1	6.44	0.28	240	-0.079	6.7
	3	08/05/88	244.7	6.55	0.39	265 ^c	-0.093	7.2
	4	08/04/88	245.3	6.55	0.13	298 ^d	-0.103	5.9
OHF	1	08/08/88	233.8	6.25	1.17	381	0.160	8.6
	2	08/08/88	229.9	6.15	0.97	265	0.017	7.3
	3	08/09/88	230.2	6.28	2.15	228	0.213	6.3
	4	08/09/88	231.1	5.46	0.56 ^d	79	0.018	1.5

^aField measurements taken during sample collection using a flow through cell connected to a Hydrolab Corporation Model Surveyor II monitoring instrument. The readings of ORP (oxygen reduction potential) were made directly from the Surveyor II instrument. (No corrections of -0.270 V were made between reference and hydrogen electrodes.) All measurements are the means of four observations except where noted.

^bDuplicate titrations using 0.01 N HCl as the titrant, multiply by 50 to convert alkalinity to mg/L of CaCO₃.

^cMean of three observations.

^dMean of two observations.

Table 5. Well evacuation informaton

Site	Well	Well volume	Well volume evacuated (L)	pH range (L)	Specific conductance range ($\mu\text{S}/\text{cm}$)	Comments
3513	1	2.1	23.0	6.23-6.27	560-668	Water was slightly turbid
	1A	10.6	37.0	6.69-6.64	233-225	Water was very clear
	2	4.2	11.3	6.70-6.70	710-711	Water was slightly turbid, milky white colored
	3	2.3	3.2	6.51-6.54	225-231	Water was very clear
	4	4.9	15.1	6.25-6.31	260-275	The first 2 L of water was very turbid, final water was very clear
HRE	1	23.4	29.1	6.77-6.84	175-277	Water was clear during well evacuation
	2	3.6	15.9	6.12-6.14	264-270	Water was very clear
	3	19.3	49.5	6.53-6.54	333-440	Initial water was slightly cloudy, but final water was clear
	4	15.1	30.2	6.53-6.60	583-606	Initial water appeared to have small rust particles, but final water was fairly clear
OHF	1	96.8	50.3	6.21-6.22	384-386	Water was slightly cloudy during well evacuation
	2	3.6	15.6	6.12-6.13	264-268	Water was clear during well evacuation
	3	6.8	20.0	5.96-6.23	172-215	Initial water had some suspended sediment, final water was slightly turbid
	4	11.0	24.2	5.33-5.38	77-78	Water was clear during well evacuation

3.2 GROUNDWATER ANALYSES

A summary of the groundwater analyses is presented in Table 6. Levels of constituents in Table 6 are mean values of detectable concentrations observed in groundwater sampled from wells upgradient and downgradient from the impoundment. In the case of the 3513 impoundment, the upgradient wells were designated 1 and 1A. For the other impoundments the upgradient well was well no. 1, and the downgradient wells, nos. 2, 3, and 4.

3.2.1 Anions in Groundwater

Levels of bromide, chloride, nitrate, and sulfate were detected in groundwater. Concentrations of fluoride and phosphate in groundwater at all three sites were below detection (<0.5 mg/L). Bromide was detected at one site in excess of the 0.5 mg/L detection level (0.7 mg/L in groundwater from well no. 1 at the OHF site). At the HRE site, upgradient concentrations of chloride and sulfate in groundwater were of similar magnitude to those concentrations downgradient from the impoundment, indicating that the impoundment was not a source of these anions in the groundwater. The same can be said for the OHF site: concentrations of chloride, nitrate, and sulfate in groundwater upgradient and downgradient from the impoundment appeared to be similar. On the other hand, at the 3513 site the mean concentration of chloride in groundwater from the downgradient wells was approximately 3 times the level observed in the groundwater from the two upgradient wells, reflecting the leaching of chloride from this impoundment. An opposite relationship was observed with respect to sulfate at this site: that is, a mean concentration in the upgradient groundwater was approximately 3 times higher than the mean concentration in the groundwater

downgradient from the 3513 impoundment. Groundwater concentrations of sulfate at this site indicate a source of sulfate upgradient from the 3513 site. Anion concentrations measured in groundwater from all wells at the three sites are presented in Table 7 (including detection levels and all data).

Table 6. Summary of groundwater analyses at each site*

		Site											
		HRE				OHF				3513			
		Well location				Well location				Well location			
		Downgradient		Upgradient		Downgradient		Upgradient		Downgradient		Upgradient	
		Result		Result		Result		Result		Result		Result	
		Mean	N	Mean	N	Mean	N	Mean	N	Mean	N	Mean	N
		Type analyses	Analysis										
Anions (mg/L)	Br	0.700	1
	Cl	6.600	3	5.800	1	12.770	3	17.000	1	32.400	4	9.350	2
	NO3	.	.	0.900	1	5.200	3	4.100	1
	SO4	42.333	3	42.000	1	20.000	3	23.000	1	18.250	4	65.500	2
Metals (ng/L)	Ag	1	0.007	3	.	.
	Al	0.655	6	0.330	2	0.355	6	1.592	2	0.409	8	0.500	4
	B	0.086	2	.	.	0.146	2	.	.	0.142	4	.	.
	Ba	0.088	6	0.066	2	0.135	6	0.280	2	0.221	8	0.104	4
	Be	0.002	6	0.002	2	0.002	6	0.003	2	0.002	8	0.003	4
	Ca	118.333	6	86.000	2	91.583	6	191.000	2	105.125	8	137.500	4
	Co	0.005	3	0.003	1	0.003	4	.	.
	Cr	0.022	2	0.006	1	0.008	1	.	.
	Cu	0.021	2
	Fe	0.992	6	.	.	0.163	3	1.618	2	1.757	8	0.782	4
	K	2.300	3	1.600	1	2.800	4	2.900	1
	Mg	19.667	6	13.000	2	7.458	6	18.650	2	17.212	8	24.250	4
	Mn	0.522	6	.	.	0.127	6	0.289	1	3.575	8	1.710	4

*Only those concentrations above analytical detection levels are listed.

Table 6. (Continued)

		Site											
		HRE				OHF				3513			
		Well location				Well location				Well location			
		Downgradient		Upgradient		Downgradient		Upgradient		Downgradient		Upgradient	
		Result		Result		Result		Result		Result		Result	
		Mean	N	Mean	N	Mean	N	Mean	N	Mean	N	Mean	N
		Type analyses	Analysis										
Metals (ng/L)	Na	14.550	6	6.950	2	24.550	6	12.650	2	33.875	8	15.250	4
	Ni	0.017	1	.	.	0.007	3	0.006	1	0.008	1	.	.
	Si	9.600	6	4.050	2	6.730	6	10.075	2	5.500	8	4.550	4
	Sr	0.268	6	0.125	2	0.142	6	0.273	2	0.626	8	0.310	4
	Ti	0.029	1	0.033	1
	V	0.009	6	0.009	2	0.006	4	0.009	2	0.009	8	0.010	4
	Zn	0.009	1	.	.	0.014	2	0.016	1	.	.	0.072	2
Organics (µg/L)	Carbon tetrachloride	121.667	3	162.000	1
	Chloroform	.	.	8.000	1	34.667	3	77.000	1
	Toluene	8.000	1
	Trichloroethene	30.000	1	19.000	1	13.500	2	19.000	1	.	.	30.000	1
	Vinyl chloride	27.667	3	.	.
	1,1-Dichloroethane	13.000	1	6.000	1
	1,1,1-Trichloroethane	12.500	2	15.000	1

Table 6. (Continued)

		Site											
		HRE				OHF				3513			
		Well location				Well location				Well location			
		Downgradient		Upgradient		Downgradient		Upgradient		Downgradient		Upgradient	
		Result		Result		Result		Result		Result		Result	
		Mean	N	Mean	N	Mean	N	Mean	N	Mean	N	Mean	N
		Type analyses	Analysis										
Organics ($\mu\text{g/L}$)	1,2-Dichloroethane	7.000	1
	1,2-Dichloroethene (total)	11.000	2	13.000	1	5.000	1	.	.	311.000	3	254.500	2
Radionuclides (Bq/L)	C-14	58.500	2	10.000	1	91000	2	66000	1	1255	4	1550	2
	Co-60	1.350	2
	Cs-137	6.300	1
	Gross alpha	0.775	2	0.077	1	0.040	3	0.086	1	0.274	3	0.155	2
	Gross beta	1206.87	3	0.340	1	1338.07	3	4.200	1	42.000	4	23.800	2
	H-3	97.333	3	28.000	1	128000	3	130000	1	2225	4	2750	2
	Sr-90	369.622	3	2.400	1	468.167	3	3.900	1	16.750	4	8.050	2
	Tc-99	1.743	3	0.066	1	1.770	3	1.100	1	0.663	3	0.730	2

Table 7. Concentrations of anions in groundwater^a

Site	Analysis in mg/L	Well				
		1	1A	2	3	4
		Result	Result	Result	Result	Result
HRE	Br	-0.5	.	-0.5	-0.5	-0.5
	Cl	5.8	.	6.5	6.1	7.2
	F	-0.5	.	-0.5	-0.5	-0.5
	NO3	0.9	.	-0.5	-0.5	-0.5
	PO4	-0.5	.	-0.5	-0.5	-0.5
	SO4	42.0	.	57.0	41.0	29.0
	OHF	Br	0.7	.	-0.5	-0.5
Cl		17.0	.	25.0	8.6	4.7
F		-0.5	.	-0.5	-0.5	-0.5
NO3		4.1	.	5.1	9.4	1.1
PO4		-0.5	.	-0.5	-0.5	-0.5
SO4		23.0	.	13.0	25.0	22.0
3513		Br	-0.5	-0.5	-0.5	-0.5
	Cl	9.0	9.7	50.5	23.0	5.6
	F	-0.5	-0.5	-0.5	-0.5	-0.5
	NO3	-0.5	-0.5	-0.5	-0.5	-0.5
	PO4	-0.5	-0.5	-0.5	-0.5	-0.5

^aNegative values denote detection level, includes all data

Table 7. (Continued)

		Well				
		1	1A	2	3	4
		Result	Result	Result	Result	Result
Site	Analysis in mg/L					
3513	SO4	87.0	44.0	25.5	8.1	13.9

3.2.2 Metals in Groundwater

Mean concentrations of metals in Table 6 include dissolved and total forms of metals [i.e., analyses by ICP using EPA method 200.7 of the filtered (0.45 μm) and nonfiltered groundwater, respectively]. Differences between dissolved and total metals in groundwater will be addressed later. Casual observation of Table 6 indicates no major trend in metals concentrations between groundwater sampled in downgradient and upgradient wells. One exception might be sodium, where it appears that concentrations are higher in groundwater from downgradient wells than from upgradient wells. Differences between concentrations of metals in groundwater taken from downgradient and upgradient wells were statistically compared by using an analysis-of-variance procedure (SAS 1985). Significantly (5% level) higher concentrations of Ba, Be, Ca, Mg, Na, and Si were observed in groundwater sampled from wells downgradient from the HRE impoundment than in groundwater sampled upgradient from the impoundment. At the OHF site statistically significant differences (5% level) were noted between the concentrations of Al, Ba, Mg, and V between groundwater sampled at wells upgradient and downgradient from the impoundment. However, in this case the groundwater from the upgradient well contained higher concentrations of metals than water from the downgradient wells. These data indicate that a likely source of such metals in the groundwater is the leaching of wastes buried in SWSA-5. At the 3513 site significant differences between downgradient and upgradient groundwater concentrations of Al, Be, Mn, Na, and Si were observed. Concentrations of Al and Be were higher in groundwater from the upgradient well whereas concentrations of Mn, Na, and Si were observed to be higher in water from the wells downgradient from the impoundment.

Concentrations of metals were determined in both filtered (groundwater passing a 0.45- μm -diam pore-size membrane filter) and unfiltered groundwater. For the purposes of this report the results are described as dissolved and total metals, respectively. Mean concentrations of dissolved and total metals (those above analytical detection level) in

groundwater sampled at all wells at the three sites are presented in Table 8. Visual comparison of dissolved and total metal mean concentrations for individual metals indicate little difference between the two analyses. One exception might be iron analyses where the mean concentration for total iron (1.939 mg/L) was considerably higher than the mean concentration observed for dissolved iron (0.985 mg/L). However, statistical analysis by an analysis-of-variance procedure (SAS 1985) revealed this difference not to be statistically significant at the 5% level. Only in the case of zinc was there a significant difference between dissolved and total concentrations (0.130 mg/L of dissolved zinc as compared to 0.003 mg/L of total zinc). However in this case only 1 groundwater sample out of 14 (well no. 1 at the 3513 site) contained detectable dissolved zinc concentrations, compared to 5 groundwater samples that contained detectable total zinc concentrations. Thus, in this instance the single analysis of 0.130 mg/L of dissolved zinc appears to be an outlier (as a result of contamination) or an error in analytically determining zinc in that sample. To further test the comparison between dissolved and total metal analyses, an analysis of variance was conducted on the data set, where an estimate in the concentration of the metal was made by using the assumption that the concentration was one-half the detection limit. In this manner, a statistical comparison is made on an equal number of observations for both the dissolved and total metal concentration. Using this approach, there was no statistical difference observed between dissolved or total metal analysis for any metal. Thus, based on these data and statistical analyses, there was no difference between filtered and nonfiltered groundwater samples. Concentrations of detectable levels of metals (dissolved and total) for each of the wells at the three sites are presented in Table 9.

Table 8. Differences between dissolved and total metal analyses
in groundwater averaged over all sites

Analysis in mg/L	Metal form					
	Dissolved			Total		
	Result			Result		
	Mean	Std	N	Mean	Std	N
Ag	0.007	0.000	2	0.006	.	1
Al	0.419	0.116	14	0.665	0.661	14
B	0.129	0.032	4	0.129	0.026	4
Ba	0.150	0.116	14	0.152	0.115	14
Be	0.002	0.000	14	0.002	0.000	14
Ca	116.714	39.783	14	112.179	42.976	14
Co	0.004	0.002	4	0.004	0.002	4
Cr	0.038	.	1	0.007	0.001	3
CU	.	.	.	0.021	0.007	2
Fe	0.985	2.006	11	1.336	1.939	12
K	2.511	0.744	9	.	.	.
Mg	17.217	6.872	14	15.694	6.853	14
Mn	1.679	1.786	12	1.498	1.634	13
Na	22.421	12.162	14	20.850	11.537	14
Ni	0.012	0.008	2	0.007	0.001	4
Si	6.804	2.554	14	6.655	2.953	14
Sr	0.346	0.287	14	0.333	0.285	14

Table 8. (Continued)

Analysis in mg/L	Metal form					
	Dissolved			Total		
	Result			Result		
	Mean	Std	N	Mean	Std	N
Ti	.	.	.	0.031	0.003	2
V	0.009	0.002	13	0.009	0.001	13
Zn	0.130	.	1	0.014	0.003	5

Table 9. Concentrations of metals in groundwater

Site	Analysis in mg/L	Metal form	Well				
			1	1A	2	3	4
			Result	Result	Result	Result	Result
HRE	Al	Dissolved	0.340	.	0.450	0.420	0.410
		Total	0.320	.	1.700	0.440	0.510
	B	Dissolved	.	.	0.082	.	.
		Total	.	.	0.091	.	.
	Ba	Dissolved	0.061	.	0.090	0.078	0.093
		Total	0.072	.	0.100	0.079	0.091
	Be	Dissolved	0.002	.	0.002	0.002	0.002
		Total	0.002	.	0.002	0.002	0.002
	Ca	Dissolved	91.000	.	130.000	120.000	110.000
		Total	81.000	.	120.000	120.000	110.000
	Cr	Dissolved	.	.	.	0.038	.
		Total	.	.	0.006	.	.
	Fe	Dissolved	.	.	0.290	1.300	0.340
		Total	.	.	2.100	1.400	0.520
	Mg	Dissolved	16.000	.	21.000	20.000	19.000
		Total	10.000	.	21.000	19.000	18.000
	Mn	Dissolved	.	.	1.300	0.090	0.180
		Total	.	.	1.300	0.082	0.180

Table 9. (Continued)

Site	Analysis in mg/L	Metal form	Well				
			1	1A	2	3	4
			Result	Result	Result	Result	Result
HRE	Na	Dissolved	7.400	.	12.000	26.000	6.500
		Total	6.500	.	11.000	26.000	5.800
	Ni	Dissolved	.	.	.	0.017	.
		Total	.	.	.	0.017	.
	Si	Dissolved	4.300	.	8.300	13.000	7.100
		Total	3.800	.	9.500	13.000	6.700
	Sr	Dissolved	0.130	.	0.200	0.400	0.220
		Total	0.120	.	0.190	0.400	0.200
	Ti	Total	.	.	0.029	.	.
		Total	.	.	0.029	.	.
	V	Dissolved	0.009	.	0.010	0.008	0.009
		Total	0.008	.	0.010	0.009	0.009
	Zn	Total	.	.	0.009	.	.
		Total	.	.	0.009	.	.
OHF	Al	Dissolved	0.584	.	0.509	0.412	0.103
		Total	2.600	.	0.510	0.458	0.136
	B	Dissolved	.	.	0.145	.	.
		Total	.	.	0.147	.	.
	Ba	Dissolved	0.258	.	0.188	0.137	0.076
		Total	0.302	.	0.176	0.161	0.075
	Be	Dissolved	0.003	.	0.002	0.002	0.001
		Total	0.003	.	0.002	0.002	0.001

Table 9. (Continued)

			Well					
			1	1A	2	3	4	
			Result	Result	Result	Result	Result	
Site	Analysis in mg/L	Metal form						
OHF	Be	Total	0.003	.	0.003	0.002	0.001	
	Ca	Dissolved	174.000	.	156.000	109.000	18.000	
		Total	208.000	.	144.000	106.000	16.500	
	Co	Dissolved	.	.	0.003	0.006	.	
		Total	0.003	.	.	0.007	.	
	Cr	Total	0.006	
	Fe	Dissolved	0.067	.	.	0.121	.	
		Total	3.170	.	.	0.261	0.107	
	K	Dissolved	1.600	.	1.900	1.800	3.200	
	Mg	Dissolved	18.100	.	9.710	8.430	4.800	
		Total	19.200	.	9.370	8.110	4.330	
	Mn	Dissolved	.	.	0.014	0.120	0.158	
		Total	0.289	.	0.015	0.130	0.324	
	Na	Dissolved	13.000	.	17.100	37.600	21.300	
		Total	12.300	.	15.600	34.800	20.900	
	Ni	Dissolved	.	.	.	0.006	.	
		Total	0.006	.	0.008	0.006	.	
	Si	Dissolved	9.050	.	9.260	8.060	3.490	

Table 9. (Continued)

			Well						
			1	1A	2	3	4		
			Result	Result	Result	Result	Result		
Site	Analysis in mg/L	Metal form							
OHF	Si	Total	11.100	.	8.540	7.770	3.260		
	Sr	Dissolved	0.258	.	0.212	0.155	0.068		
		Total	0.288	.	0.204	0.152	0.060		
	Ti	Total	0.033		
	V	Dissolved	0.008	.	0.007	0.005	.		
		Total	0.010	.	0.007	0.005	.		
	Zn	Total	0.016	.	0.016	0.012	.		
	3513	Ag	Dissolved	.	.	0.007	.	.	
			Total	.	.	0.006	.	.	
		Al	Dissolved	0.540	0.500	0.355	0.420	0.470	
Total			0.490	0.470	0.380	0.430	0.480		
B		Dissolved	.	.	0.145	.	.		
		Total	.	.	0.140	.	.		
Ba		Dissolved	0.140	0.075	0.390	0.066	0.057		
		Total	0.130	0.072	0.375	0.066	0.053		
Be		Dissolved	0.002	0.003	0.002	0.002	0.002		
		Total	0.002	0.003	0.002	0.002	0.002		
Ca		Dissolved	170.000	120.000	88.000	120.000	140.000		

Table 9. (Continued)

Site	Analysis in mg/L	Metal form	Well				
			1	1A	2	3	4
			Result	Result	Result	Result	Result
3513	Ca	Total	150.000	110.000	82.500	110.000	130.000
	Co	Dissolved	.	.	0.003	.	.
		Total	.	.	0.003	.	.
	Cr	Total	.	.	0.008	.	.
	CU	Total	0.016	0.026	.	.	.
	Fe	Dissolved	0.740	0.920	0.029	6.900	0.094
		Total	0.770	0.700	0.073	6.700	0.160
	K	Dissolved	2.900	.	3.400	2.600	1.800
	Mg	Dissolved	26.000	25.000	24.000	9.000	16.000
		Total	23.000	23.000	23.000	8.700	10.000
	Mn	Dissolved	3.200	0.280	4.400	3.200	2.800
		Total	3.100	0.260	4.150	2.900	2.600
	Na	Dissolved	19.000	14.000	43.000	26.000	28.000
		Total	16.000	12.000	40.000	25.000	26.000
	Ni	Total	.	.	0.008	.	.
	Si	Dissolved	4.100	5.600	5.500	5.400	6.600
		Total	3.600	4.900	5.100	5.000	5.800
	Sr	Dissolved	0.310	0.340	0.990	0.250	0.320

Table 9. (Continued)

			Well				
			1	1A	2	3	4
			Result	Result	Result	Result	Result
Site	Analysis in mg/L	Metal form					
3513	Sr	Total	0.280	0.310	0.975	0.230	0.280
		V	Dissolved	0.008	0.011	0.010	0.008
		Total	0.009	0.011	0.009	0.008	0.009
	Zn	Dissolved	0.130
		Total	.	0.015	.	.	.

3.2.3 Organic Compounds in Groundwater

Analyses of groundwater samples revealed quantitative concentrations of eight organic compounds (carbon tetrachloride, chloroform, toluene, trichloroethene, vinyl chloride, 1,1-trichloroethane, 1,2-dichloroethane, and 1,2-dichloroethene; see Table 6). The most prevalent were carbon tetrachloride and chloroform at the OHF site and 1,2-dichloroethene at the 3513 site (namely, these organic compounds were measured quantitatively in all groundwater samples taken at these sites). Levels of trichloroethene as well as 1,1-di-chloroethane and 1,1,1-trichloroethane were also measured in the upgradient and downgradient groundwater at the OHF impoundment. However, the data do not indicate any of the impoundments are sources of these organic compounds in groundwater. For example, concentrations of each of the above-listed organic compounds were observed in both upgradient and downgradient groundwater samples at concentrations that were not statistically different (tested at the 5% level, except in the case of 1,1-dichloroethane which was detected in the upgradient and one downgradient well at the OHF site). At the OHF site the likely source of organic compounds, principally carbon tetrachloride and chloroform, is the leaching of wastes buried in SWSA-5 which is upgradient hydrologically from OHF site. Also, the 1,2-dichloroethane (which is a degradation product of trichloroethane) observed in groundwater at the 3513 site likely resulted from transport from a source upgradient from the impoundment. Thus, these data imply that the impoundments are not sources of organic compounds leaching to the groundwater. One exception might be the case of vinyl chloride at the 3513 site. In this instance, vinyl chloride (another degradation product of trichloroethane) was measured in groundwater from all three wells downgradient from the impoundment (mean concentration of 28 $\mu\text{g/L}$), while its concentration was below quantifying levels in groundwater sampled upgradient from the impoundment.

Concentrations of carbon tetrachloride and chloroform (Table 6) in groundwater downgradient as well as upgradient from the OHF impoundment are well above the proposed RCRA reference level of 5 $\mu\text{g/L}$ in drinking water (51 FR 21648-21693 and 50 FR 46880, cited by Trabalka, 1987). Also, the mean concentration of vinyl chloride (27.7 $\mu\text{g/L}$) observed in the groundwater downgradient from the 3513 impoundment is far above the proposed RCRA reference level of 1 $\mu\text{g/L}$. Levels of organic compounds detected in groundwater sampled at each of the monitoring wells at the individual impoundment sites are listed in Table 10.

3.2.4 Radionuclides in Groundwater

As mentioned in the background section, previous groundwater monitoring efforts had shown significant leaching of radionuclides from the impoundments; especially ^{90}Sr . Monitoring in 1988 confirmed this finding, as well as verified the very high concentrations of tritium (>100,000 Bq/L) previously observed in the groundwater from both the downgradient and upgradient monitoring wells at the OHF site. At the 3513 impoundment moderately high levels of tritium in groundwater were also observed in water from both the upgradient and downgradient wells (concentrations on the order of 2,500 Bq/L). Gross alpha and gross beta activities in the groundwater were similar to those determined in the past. As outlined in Section 2, because concentrations of gross alpha activity were <2 Bq/L, analyses for individual alpha-emitting radionuclides were not performed.

One surprise in the 1988 sampling and analysis was the high concentrations of ^{14}C (70,000 to 90,000 Bq/L) measured in the groundwater upgradient as well as downgradient from the OHF impoundment (Table 6 and 11). There was no statistically significant difference in upgradient and downgradient ^{14}C levels (tested at the 5% level). ^{14}C was not determined in groundwater from monitoring well no. 4 because of the interference from the high levels of gross beta activity, presumably due to the high levels of ^{90}Y and ^{90}Sr . Moderately high levels of ^{14}C (700 to 2,600 Bq/L)

were also observed in groundwater at the 3513 site. Low levels of ^{14}C were detected in groundwater at the HRE site (10 and 100 Bq/L in the upgradient and downgradient groundwater, respectively). Technetium-99 was also detected in groundwater at all three sites; however, it was found in relatively low concentrations (0.07 to 1.74 Bq/L). The presence of ^{14}C or ^{99}Tc in the groundwater at these sites had not been detected in the earlier groundwater investigations. Comparison of radionuclide concentrations in groundwater upgradient and downgradient from the impoundments revealed that ^{90}Sr is the only radionuclide whose concentrations in groundwater reflects leaching from the impoundments (see Table 6). However, even the large differences in mean ^{90}Sr concentrations in groundwater from downgradient wells as compared to water from upgradient wells at the HRE and OHF impoundments (370 versus 2.4 Bq/L and 468 versus 3.9 Bq/L, respectively) did not test statistically different at the 5% level. The large variability in concentrations of ^{90}Sr in groundwater from the downgradient wells is largely responsible for not showing a statistical difference between the upgradient and downgradient concentrations. For example, groundwater concentrations of ^{90}Sr from the HRE downgradient wells were 1100, 0.1, and 8.8 Bq/L, and ^{90}Sr concentrations measured in water from the downgradient wells at the OHF site were 1.3, 3.2, and 1400 Bq/L (see Table 11). The variance used to make a comparison between upgradient and downgradient concentrations is determined from the variability in concentrations among the three downgradient concentrations; thus, in many cases a statistical difference between upgradient and downgradient concentrations is not observed.

3.2.5 Analyses of Blank Samples

To evaluate analytical accuracy and potential for contamination during the sampling of groundwater at the impoundment site, seven "blank" samples were submitted to the analytical laboratory for analyses. These samples, using ASTM Type II water, were from the OHF sampling site. The

sample identification, requested analyses, and method of collection are presented in Table 12.

The only samples to contain detectable levels of the analyte were samples SB1-TM, SB1-DM, and SB1-RAD (Table 13). Minor levels of Ca, K, Mg, Mn, and Na were detected in blank samples taken at the OHF site (all <1 mg/L except for Na). However, there appears to be considerable contamination of the blank sample submitted for radionuclide analyses at the OHF site. For example, 450 Bq/L of tritium and 3.8 Bq/L of ^{90}Sr were detected. As mentioned previously, this sample was collected the day following the sampling of groundwater from No. 4 well at the OHF site which contains considerable levels of both of these radionuclides (34,000 and 1,400 Bq/L of tritium and ^{90}Sr , respectively). The method of collection is described in Table 12 (sample SB1-RAD). The levels of radionuclides observed in the blank sample indicate significant cross contamination of radionuclides after sampling the no. 4 monitoring well; however, the levels were well below that observed in the groundwater.

3.2.6 Analyses of Replicate Groundwater Samples

To estimate the combined precision in collection and analytical detection of the various analytes in groundwater, duplicate samples were taken at the 3513 site (well no. 2). Requested analytes were for anions, metals (dissolved and total), organics (volatile and semivolatile), and radionuclides. The replication between samples was very good; namely, the coefficient of variation was generally <10% (see Table 14). In certain instances, for example, iron, ^{90}Sr , and ^{99}Tc , the coefficient of variation was in excess of 25%. The good replication for the organic compounds (coefficient of variation for vinyl chloride and 1,2-dichloroethene of 5.9 and 5.1%, respectively) was outstanding, considering the very low concentrations in groundwater.

Table 10. Concentrations of organic compounds in groundwater

		Well				
		1	1A	2	3	4
		Result	Result	Result	Result	Result
Site	Analysis in µg/L					
HRE	Chloroform	8.0
	Trichloroethene	19.0	.	30.0	.	.
	1,2-Dichloroethene (total)	13.0	.	8.0	.	14.0
OHF	Carbon Tetrachloride	162.0	.	22.0	214.0	129.0
	Chloroform	77.0	.	33.0	54.0	17.0
	Trichloroethene	19.0	.	8.0	19.0	.
	1,1-Dichloroethane	6.0	.	13.0	.	.
	1,1,1-Trichloroethane	15.0	.	10.0	15.0	.
	1,2-Dichloroethane	.	.	7.0	.	.
	1,2-Dichloroethene (total)	.	.	5.0	.	.
3513	Toluene	.	8.0	.	.	.
	Trichloroethene	30.0
	Vinyl chloride	.	.	24.0	35.0	.

Table 10. (Continued)

		Well				
		1	1A	2	3	4
		Result	Result	Result	Result	Result
Site	Analysis in μg/L					
3513	1,2- Dichloroethene (total)	472.0	37.0	459.5	14.0	.

3.2.7 Analyses of Spiked Water Samples

To assess accuracy in the determination of radionuclides and metals in groundwater, water samples (ASTM Type II) were spiked with quantities of standard water samples. The metal standards were obtained from the National Bureau of Standards and the radionuclide standards were obtained from EPA's Environmental Monitoring Systems Laboratory, Las Vegas, Nevada. The comparison between known and observed concentrations of radionuclides and metals is presented in Tables 15 and 16. In the spiked radionuclide sample, ^{60}Co and ^{134}Cs were not detected. Other than the gross beta comparison, the remainder of the analyses were not in large error. Observed metal concentrations generally were lower than the known concentrations. However, taking into consideration the relatively low levels (all but iron and strontium were <0.1 mg/L), the differences between observed and known concentrations should not be a major concern for this study.

Table 11. Concentrations of radionuclides in groundwater^a

Site	Analysis in Bq/L	Well				
		1	1A	2	3	4
		Result	Result	Result	Result	Result
HRE	C-14	10.0	.	.	100.0	17.0
	Co-60	-0.2	.	-0.3	-0.2	-0.1
	Cs-137	-0.2	.	-0.2	-0.2	-0.2
	Gross alpha	0.1	.	1.4	0.0	0.1
	Gross beta	0.3	.	3600.0	0.6	20.0
	H-3	28.0	.	39.0	230.0	23.0
	Sr-90	2.4	.	1100.0	0.1	8.8
	TC-99	0.1	.	0.5	3.3	1.4
OHF	C-14	66000	.	93000	89000	.
	Co-60	-0.4	.	-0.9	1.7	1.0
	Cs-137	-0.5	.	-0.5	-0.7	6.3
	Gross alpha	0.1	.	0.1	0.0	0.1
	Gross beta	4.2	.	1.2	13.0	4000.0
	H-3	130000	.	180000	170000	34000
	Sr-90	3.9	.	1.3	3.2	1400.0
	TC-99	1.1	.	0.9	3.5	0.9
3513	C-14	700.0	2400.0	710.0	1000.0	2600.0

^aNegative values denote detection level, includes all data.

Table 11. (Continued)

		Well				
		1	1A	2	3	4
		Result	Result	Result	Result	Result
Site	Analysis in Bq/L					
3513	Co-60	-0.7	-0.1	-0.6	-0.7	-1.0
	Cs-137	-0.7	-0.2	-0.6	-0.7	-0.6
	Gross alpha	0.1	0.2	0.4	0.1	0.0
	Gross beta	38.0	9.6	79.0	2.6	7.4
	H-3	1300.0	4200.0	1300.0	1800.0	4500.0
	Sr-90	13.0	3.1	31.0	2.6	2.4
	Tc-99	1.2	0.3	0.4	0.3	0.9

Table 12. Method of preparation of blank water samples

Sample ID	Requested analyses	Method of collection
SBI-TM-S	Total metals	Water was passed through the Telfon tubing and stainless steel manifold used for sampling the first two wells (no. 1 and 1A) at the 3513 site
SBI-TM	Total metals	Water was passed through the Telfon tubing and high-density PVC manifold used during sampling and acidified with nitric acid at the OHF site
SBI-VO	Volatile organics	Water was passed through the Telfon tubing used during sampling at the OHF site
SBI-SVO	Semivolatile organics	Water was passed through the Telfon tubing used during sampling at the OHF site.
SBI-DM	Dissolved metals	Water was passed through the Telfon tubing and high-density PVC manifold used during sampling, filtered and acidified with nitric acid at the OHF site
SBI-1	Anions	Water was passed through the Telfon tubing and high-density PVC manifold used during sampling at the OHF site
SBI-RAD	Radionuclides	Water was passed through the Telfon tubing and high-density PVC manifold used during sampling and acidified with nitric acid at the OHF site

OHF = Old Hydrofracture Facility.

Table 13. Concentrations in blank samples^a

			Result
TYPE	SAMPLE	Analysis	
Metals (mg/L)	SBI-TH	Mg	0.013
		Zn	0.018
	SBI-DM	Ca	0.225
		K	0.200
		Mg	0.056
		Mn	0.006
		Na	1.570
Radio- nuclides (Bq/L)	SBI-RAD	Gross alpha	0.002
		Gross beta	1.100
		H-3	450.000
		Sr-90	3.800
		Tc-99	0.180

^aAnalyses below analytical detection levels are not reported.

Table 14. Comparison between replicate sampling at the 3513 well no. 2^a

		Replicate		Result		
		A	B			
		Result	Result			
		Mean	Mean			
Type	Analysis					
Anion (mg/L)	Cl	53.000	48.000	50.500	7.0	2.0
	SO ₄	26.000	25.000	25.500	2.8	2.0
Metal (mg/L)	Ag	0.007	0.007	0.007	9.2	3.0
	Al	0.345	0.390	0.367	11.8	4.0
	B	0.145	0.140	0.142	3.5	4.0
	Ba	0.380	0.385	0.382	2.5	4.0
	Be	0.002	0.002	0.002	2.2	4.0
	Ca	84.500	86.000	85.250	4.0	4.0
	Co	0.003	0.003	0.003	16.2	4.0
	Cr	.	0.008	0.008	.	1.0
	Fe	0.033	0.070	0.051	76.0	4.0
	K	3.400	3.400	3.400	0.0	2.0
	Mg	23.500	23.500	23.500	2.5	4.0
	Mn	4.250	4.300	4.275	3.5	4.0
	Na	41.500	41.500	41.500	4.2	4.0
	Ni	.	0.008	0.008	.	1.0
	Si	5.250	5.350	5.300	4.6	4.0
Sr	0.985	0.980	0.982	1.3	4.0	

^aAnalyses below analytical detection levels are not reported.

Table 14. (Continued)

		Replicate		Result		
		A	B			
		Result	Result			
		Mean	Mean			
Type	Analysis					
Metal	V	0.010	0.010	0.010	3.4	4.0
Organic (µg/L)	vinyl chloride	25.000	23.000	24.000	5.9	2.0
	1,2-dichloroethene (total)	476.000	443.000	459.500	5.1	2.0
Radionuclides (Bq/L)	C-14	730.000	690.000	710.000	4.0	2.0
	Gross alpha	0.340	0.420	0.380	14.9	2.0
	Gross beta	80.000	78.000	79.000	1.8	2.0
	H-3	1300	1300	1300	0.0	2.0
	Sr-90	37.000	25.000	31.000	27.4	2.0
	Tc-99	0.000	0.740	0.370	141.4	2.0

Table 15. Radioisotopic analyses of spiked water samples

Analyte	Known concentration (Bq/L)	Observed concentration (Bq/L)	Counting error ^a	Difference ^b (%)
⁶⁰ Co	0.55	<1	NA ^c	NA
⁶⁵ Zn	3.71	4.5	1.8	21
¹⁰⁶ Ru	7.17	10	1	39
¹³⁴ Cs	0.74	ND ^d	NA	NA
¹³⁷ Cs	0.92	0.23	0.53	-75
⁹⁰ Sr	0.74	0.68	0.23	-8
³ H	929	660	70	-29
Gross alpha	0.55	0.42	0.2	-24
Gross beta	0.15	0.78	0.22	430
Mean difference for radioisotopes				50

NA = not applicable; ND = concentration not detected.

^aCounting error is two standard deviations.

^bDifference defined as $\% = 100 \times (OC - KC) / KC$ where OC is observed concentration and KC is known concentration.

Table 16. Metallic analyses of spiked water samples

Analyte	Known concentration ($\mu\text{g/L}$)	Observed concentration ($\mu\text{g/L}$)	Difference* (%)
Ag	10	7.4	-26
Ba	45	30.7	-32
Be	19	14.5	-24
Cd	20	13.8	-31
Co	26	18.8	-28
Cr	18.9	16.1	-15
Cu	22.3	21.5	-4
Fe	101	114	13
Mn	28	22.4	-20
Mo	86	64.6	-25
Ni	50	31.8	-36
Pb	24.1	<30	NA
Se	9.9	<5	NA
Sr	231	159	-31
Tl	8.1	ND	NA
V	46	34.4	-25
Zn	67	62.9	-6
Mean difference for metals			-17

NA = not applicable; ND = concentration not detected.

*Difference defined as $\% = 100 \times (\text{OC} - \text{KC}) / \text{KC}$ where OC is observed concentration and KC is known concentration.

4. SUMMARY AND CONCLUSIONS

Groundwater monitoring at three ORNL inactive waste impoundments during July and August of 1988 confirmed earlier findings that the major contaminants entering groundwater as a consequence of these waste impoundments are radionuclides, principally ^{90}Sr . The major difference between groundwater monitoring in 1988 and the three previous years was the emphasis in 1988 to determine if hazardous organic compounds, namely volatile and semivolatile organics, were leaching into the groundwater from these impoundments. Previous monitoring had been limited to analyses of groundwater for total organic carbon (TOC) and total organic halogens (TOX), based on guidelines established in Title 40, CFR (Subpart F, Groundwater Protection, paragraph 265.92). Two radionuclides, ^{99}Tc and ^{14}C , were also included in the 1988 analyses of groundwater. These radionuclides were not measured in groundwater in previous monitoring, but were included in the 1988 analyses because they would not have been detected in the method used to determine gross beta activity.

Detectable levels of organic compounds were measured in groundwater at all three impoundments. Relatively large concentrations of carbon tetrachloride and chloroform (22 to 214 $\mu\text{g/L}$ and 17 to 77 $\mu\text{g/L}$, respectively) were measured in groundwater sampled from all monitoring wells at the OHF site. Mean concentrations of carbon tetrachloride and chloroform in water taken from the OHF downgradient wells were not statistically different from the concentrations measured in the upgradient well, indicating that the source of the compounds leaking into groundwater is likely wastes buried in SWSA-5 located upgradient from the OHF impoundment. Trichloroethene as well as 1,1-dichloroethane and 1,1,1-trichloroethane were also detected in the upgradient and downgradient groundwater at the OHF site. Concentrations of 1,2-dichloroethane (known to be a degradation product of trichloroethane contained in machining solvents and degreasers) were observed in groundwater sampled from both the downgradient as well as the upgradient wells at 3513, indicating likely contamination from a source upgradient from the impoundment.

In general, organic compounds were detected in water sampled from wells upgradient and wells downgradient from the impoundment site indicating that the impoundments are not sources of organic compounds leaching into groundwater. One exception was the OHF site, where vinyl chloride was detected in groundwater from all three wells downgradient from the impoundment, while its concentration was below detection in groundwater sampled from the monitoring well upgradient from the impoundment.

Concentrations of metals, as measured by inductively coupled plasma spectroscopy (ICP), were determined in both filtered (groundwater passing a 0.45- μm -diam pore-size membrane filter) and unfiltered groundwater. Statistical analysis by an analysis-of-variance procedure revealed no significant differences (at the 5% probability level) between concentrations of metals in filtered and nonfiltered groundwater samples at any of the impoundment sites. Anion concentrations in groundwater, as measured by ion chromatograph, were dominated by sulfate and chloride. Sulfate and chloride concentrations in groundwater ranged from approximately 5 to 50 mg/L. At the HRE and OHF sites, concentrations in groundwater from wells upgradient from the impoundments contained levels similar in magnitude to groundwater sampled from wells downgradient from the impoundment, indicating the impoundments not to be a source of these anions to groundwater. At the 3513 impoundment groundwater from the downgradient wells contained on the order of 3 times more chloride than that measured in the upgradient monitoring wells, indicating that chloride is leaking from this impoundment. On the other hand, sulfate concentrations in groundwater taken from the wells upgradient from the 3513 site were approximately 3 times the levels in the groundwater from the wells downgradient from the site, showing that the source of sulfate in groundwater is upgradient from the 3513 site. Levels of bromide, fluoride, phosphate, and nitrate in groundwater were generally below analytical detection (0.5 mg/L).

Concentrations of radionuclides in groundwater at the three sites were similar to those reported by Francis and Stansfield (1986). The major surprise was the high levels of ^{14}C detected in groundwater at the OHF

site. The source of ^{14}C in groundwater is assumed to be ^{14}C leaching from wastes buried in SWSA-5. For example, approximately 70,000 Bq/L of ^{14}C were measured in the groundwater from the monitoring well upgradient from the impoundment. On the other hand, approximately 90,000 Bq/L were observed in groundwater from two of the monitoring wells downgradient from the impoundment, raising the possibility that the impoundment might be another source of ^{14}C to groundwater. However, ^{14}C levels in upgradient and downgradient groundwater were not statistically different (tested at the 5% level). It would be interesting and advisable to characterize the form of ^{14}C measured in groundwater at the OHF site. For example, is the ^{14}C associated with soluble carbonates in groundwater or could ^{14}C be associated with the levels of organic compounds measured in groundwater at this site, namely, ^{14}C -labeled carbon tetrachloride or chloroform? Detectable levels of ^{14}C were also observed in groundwater taken from both upgradient and downgradient wells at the HRE and 3513 sites, indicating ^{14}C contamination from upgradient sources at these sites as well.

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A.1. MEASUREMENT OF STATIC DEPTH TO WATER IN MONITORING WELLS

A.1.1 Introduction

If it is determined that the potential exists for the presence of immiscible organic contaminants, the presence of these contaminants must be determined and sampled if present.

This procedure also includes provisions for measurement of static water elevations in each well prior to each sampling event. Collection of water elevations on a continuing basis is important to determine if horizontal and vertical flow gradients have changed since initial site characterization. A change in hydrologic conditions may require modification to the design of the groundwater monitoring system. Normally the water level measurements include depth to standing water and total depth of the well; however, measurements of total depth are not warranted at the 3513, Old Hydrofracture Facility, and Homogeneous Reactor Experiment sites because of the difficulty in removing dedicated sampling pumps and the possibility of contaminating the pumps as they are removed. The measured water level elevation along with the total depth of the well measured during installation of the dedicated pumps will be used for the determination of the stagnant water in the well.

A.1.2 References

- Oil Recovery System, Inc., Interface Probe Manual.
- RCRA Groundwater Monitoring Technical Enforcement Guidance Document (TEGD), September 1986, OSWER-9950.1.

A.1.3 Equipment and Materials

- Teflon Quartz Interface Probe - Oil Recovery Systems, Inc.;
- Immiscible Layer and Water Level Determination Field Log sheets; and
- Cleaning solutions:
 - Nonphosphate detergent,
 - 0.1 N HCl,
 - Tap water,
 - Distilled water,
 - Acetone, and
 - Pesticide-quality hexane.

A.1.4 Use of Interface Probe to Detect Immiscible Layers and Measure Static Water Level

- Before activating the probe, attach the grounding clip to a suitable earth ground.

- Turn the unit on by unfolding the crank handle away from the reel housing. This activates a power switch inside the reel.
- Press the test button on the face plate. If the power is on, an alarm will sound, verifying that the unit is operational. NOTE: A low battery light will indicate if battery replacement is necessary. Consult the operating manual before replacing batteries. Batteries must be Duracell Type MN1500.
- Release the probe by pulling the protector tube outward from the reel casing.
- Lower the probe by tilting the front of the reel housing forward and depressing the brake release, located just forward of the handle. The tape will continue its descent as long as the brake release is depressed. Care should be taken to prevent the tape from rubbing against the well casing.
- An alarm in the reel will sound when the probe contacts liquid. An oscillating tone indicates water; a solid tone indicates hydrocarbons. If only an oscillating tone is obtained, carefully raise and lower the probe until the point at which the tone first occurs can be accurately determined. Using the top of the well casing as the reference point, read the depth to the nearest 0.01 ft from the digital readout on the reel and record the results to the nearest 0.01 ft on the Immiscible Layer and Water Level Determination sheet.
- If a solid tone is obtained, the probe should be carefully moved up and down so that the alarm goes from no tone to solid tone. Read the depth to the nearest 0.01 ft at the exact point where the tone goes solid using the top of the well casing as the reference point. Record the result to the nearest 0.01 ft on the Immiscible Layer and Water Level Determination sheet.
- Next, lower the probe until the alarm tone starts oscillating. Carefully move the probe up and down until the exact point where the tone goes from solid to oscillating is found. Read the depth at this point to the nearest 0.01 ft, using the top of the well casing as the reference point. Record the result to the nearest 0.01 ft on the Immiscible Layer and Water Level Determination sheet.
- Mark the appropriate boxes on the Immiscible Layer and Water Level Determination sheets to indicate that the well was checked for floaters and to indicate whether or not floaters were found. If floaters are present, the well must be sampled for these contaminants using the standard operation practice outlined for collection of immiscible phases in ground monitoring wells.

- After completing the measurements, snap the probe's protector tube shut so that the wiper rests against the tape. Reel in the tape, open the tube, reel the probe into the tube and close.
- Clean the probe between each well in the following manner:
 - Wash with nonphosphate detergent.
 - Rinse with 0.1 N HCl.
 - Rinse with distilled water.
 - Rinse with acetone.
 - Rinse with pesticide- quality hexane.
 - Allow to thoroughly dry.

A.2. COLLECTION OF IMMISCIBLE PHASES FROM MONITORING WELLS

A.2.1 Introduction

If present, immiscible phases must be collected before purging activities begin. The method of choice for collecting light-phase immiscibles "floaters" is dependent on the thickness of the layer and the depth to the surface of the layer. When the thickness of the floating layer is less than 2 ft, a peristaltic pump or a bailer which fills from the top will be used. If the thickness of the phase is 2 ft or greater, samples will be collected with a bottom valve bailer. Dense-phase immiscibles ("sinkers") will be collected with a bottom double check valve bailer prior to purging of the well. In all cases, care must be taken to carefully lower the bailer into the well so that minimal agitation of the immiscible layer is achieved.

A.2.2 References

- RCRA Groundwater Monitoring Technical Enforcement Guidance Document (TEGD), September 1986, OSWER-9950.1.

A.2.3 Equipment and Materials

- Teflon bailers,
- Teflon tubing,
- Teflon-coated wire,
- Double check valve bottom bailers,
- Peristaltic pump,
- Containers precleaned to EPA specifications (Commercial Supplier--I-Chem).

A.2.4 Collection of Immiscible layers

Equipment used for collecting floaters and sinkers should be cleaned prior to use in the field whenever possible. All sample containers will consist of bottles purchased precleaned to EPA specifications.

A.2.4.1 Collection of "Floater" with Peristaltic Pump

- Dedicated tubing should be used to avoid cross contamination.
- The tubing should be lowered to the midpoint of the immiscible layer, the pump turned on, and two 40-mL borosilicate vials with Teflon septums filled for volatile analysis, followed by a 1-L amber glass bottle with Teflon cap for analyses of semivolatiles. The sample flow rate must be such that minimal aeration of the sample occurs as the containers are filled.

- At no time should the tubing going into the well be allowed to touch the ground or other physical objects that might contaminate the tubing and introduce contaminants into the well.

A.2.4.2 Collection of Immiscible Layers by Bailing

- Preclean bailers and bailer line by following the procedure outlined for organic sampling in the standard operating procedure for collection of RCRA well samples.
- Wrap bailers and line in aluminum foil for transport to the field or from one site to the next.
- Carefully lower the bailer intake to the midpoint of the immiscible layer and fill the bailer while it is being held at this level. The bailer must be lowered into the immiscible layer slowly so that minimal agitation of the immiscible layer occurs. If a floater layer less than 2 ft thick is being collected, use a top filling Teflon bailer or peristaltic pump. If a floater layer greater than 2 ft thick is being collected, use the bottom filling bailer. If a sinker is being collected, use the double check valve bailer.
- At no time should the bailer or line be allowed to touch the ground or otherwise come in contact with other physical objects that might introduce contaminants into the well.

A.3. WELL EVACUATION PROCEDURE

A.3.1 Introduction

In order to ensure that the water in the well is representative of the insitu groundwater quality, the standing water in both the well and filter pack, must be removed prior to sampling. For high yielding wells, three casing volumes will be removed prior to sampling. The pH, conductivity, and temperature will be monitored during the evacuation. Once these parameters have stabilized, the well may be sampled even if three casing volumes have not been evacuated; however, greater than one casing volume will always be evacuated prior to sampling. Sampling should be undertaken within 2 h after the well has been evacuated. Whenever full recovery exceeds 2 h, each sample will be collected as soon as sufficient volume is available for each parameter. Upgradient wells (installed in the direction of increasing static head) must be evacuated and sampled first. Downgradient wells may then be evacuated and sampled after completing the upgradient wells.

A.3.2 Equipment and Materials

- Well Wizard Controller Box,
- Calculator,
- 55-gal drum for purge water,
- Hydrolab Surveyor II water quality meter,
- 1-L graduated cylinder
- Dedicated Well Wizard pumps, and
- Stop watch.

A.3.3 Calculation of Water Volume in Well

- Calculate the volume of water in the well in liters by using the formula: $\text{Volume}(V) = 0.314 \times (d/2)^2 \times h$, where d is the inside diameter of the well in cm, h is the height of the water column in meters. The inside diameter of each well is shown in Table 1 in Sect. 2 of the main report.
- Record the calculated volume on the Well Evacuation Summary sheet.

A.3.4 Well Evacuation

- Open the Well Wizard case; remove the air hose and the connectors for the battery.
- Connect the air hose to the pump supply on the Well Wizard and the other end to the connector on the inner well cap.
- Plug the power supply line into the Well Wizard and place the connectors on the 12-v battery post.
- Remove the lid from the 55-gal drum.
- Pull the exposed teflon line out of the well casing and insert the end into the 55-gal drum.
- Turn on the bladder pump to begin evacuation and record the time of initiation on the Well Evacuation Summary sheet.
- Estimate the rate of purging by measuring the amount of water per minute pumped into the 1000-mL graduated cylinder.
- Continue evacuation until three column volumes have been evacuated or until the pH, temperature, and conductivity have stabilized as outline in Sect. 3.5. Record the time that the evacuation was completed and the total volume evacuated on the Well Evacuation Summary sheet.

A.3.5 Stabilization of Field Parameters

The well can be considered to be adequately purged after (1) three casing volumes have been removed or (2) at least one casing volume has been removed and the pH, conductivity, and temperature have stabilized according to the following procedure.

- Temperature does not vary more than 0.2°C in 1 min.
- pH does not vary more than 0.1 units in 1 minute
- Conductivity does not vary by more than 5% in 1 min.

A.4. MEASUREMENT OF PH, TEMPERATURE, CONDUCTIVITY, DISSOLVED OXYGEN, AND OXIDATION REDUCTION POTENTIAL

A.4.1 Introduction

The Hydrolab Surveyor II is a portable field instrument used to measure pH, temperature, conductivity, dissolved oxygen (DO), and oxidation-reduction potential (ORP). These measurements are to be taken prior to collection of groundwater samples in order to ensure that the well has been properly evacuated. Measurements will also be taken during sampling and at the completion of sampling to verify that conditions have remained stable. Once the pH, temperature, and conductivity have stabilized the well may be sampled even if fewer than three column volumes have been evacuated. However, more than one column volume will always be evacuated prior to sampling.

A.4.2 Procedure

- Remove the Hydrolab Surveyor II and record the instrument number on the Well Evacuation Summary sheet.
- Put on gloves and begin to evacuate the well by pumping the water into the 1000-mL polyethylene graduated cylinder. Record the time and rate of evacuation on the Well Evacuation Summary sheet.
- Note the appearance of the water (color, cloudy, clear, muddy, etc.) and record the data on the Well Evacuation Summary sheet.
- Attach the flow-through cell to the pump discharge line and continue to evacuate the well.
- Set the selector dial to temperature and record the digital readout displayed on the Well Evacuation Summary sheet to the nearest 0.1°C.
- Set the selector dial to pH and record the digital readout displayed on the Well Evacuation Summary sheet to the nearest 0.1 pH units.
- Set the selector dial to conductivity and record the digital readout displayed on the Well Evacuation Summary sheet to the nearest 0.01 mS/cm.
- Set the selector dial to DO and record the digital readout displayed on the Well Evacuation Summary sheet to the nearest 0.1 mg/L.
- Set the selector dial to ORP and record the digital readout displayed on the Well Evacuation Summary sheet to the nearest 0.001 v.

- Continue to take readings until the pH, temperature, and conductivity have stabilized. These parameters may be considered stable when these conditions are met:
 - Temperature does not vary more than 0.2°C in 1 min.
 - pH does not vary more than 0.1 units in 1 min.
 - Conductivity does not vary by more than 5% in 1 min.
- Record any unusual conditions, such as discoloration of the groundwater, presence of immiscible layers, odors, highly turbid water, equipment malfunctions, or deviations from standard procedures on the Well Evacuation Summary sheet.
- Once the field parameters have stabilized or three column volumes have been removed, sample the well. (A minimum of one casing volume should always be removed even if the field parameters stabilize before one casing volume is removed.)
- All purge water is to be collected and drummed. The collected water will be kept until analytical results are available so that laboratory and field results may be utilized to determine if the water is hazardous and how to properly dispose of the water.

A.5. COLLECTION OF RCRA WELL SAMPLES

A.5.1 Introduction

Techniques used to withdraw groundwater samples from a well must be based on considerations of the parameters to be analyzed in the samples. The order of collection, collection techniques, choice of sample containers, preservatives, and equipment are all critical to ensure that samples are not physically altered or contaminated.

A.5.2 Equipment and Materials

- Appropriate sample containers,
- Appropriate sample preservatives,
- Ice and cooler,
- Field log sheets,
- Sample labels,
- Rubber gloves,
- Trash bag,
- Kimwipes,
- Kleenex,
- Wash bottle of deionized water,
- Plastic ground cover, and
- In-line filters.

A.5.3 Sample Withdrawal

This procedure applies to wells that contain a dedicated Well Wizard bladder pump for withdrawal of formation water from the well. The pump and tubing are made of stainless steel and teflon.

- Sampling should be done as soon as possible after the well has been evacuated. Sampling must be undertaken within 2 h after the well has been evacuated. If this is not possible due to insufficient recovery, a note should be made on the Well Sampling Summary sheet and the well should be sampled as soon sufficient water exists.
- Upgradient wells (installed in the direction of increasing static head) must be evacuated and sampled first.
- The Well Wizard pump will be regulated so that the water discharges in a reasonably continuous stream and does not pulsate excessively causing aeration of the sample. The maximum flow rate to be utilized for collection of volatile parameters will be 100 mL per minute. After these parameters have been collected, the flow rate may be increased to between 200 and 400 mL per minute for collection of the remaining samples. However, at no time will the rate of evacuation during sample collection equal or exceed the rate of evacuation during purging.

A.5.4 Sample withdrawal, preservation, and handling

- Samples will be collected in the following order;
 - a. Temperature, pH, conductivity, DO, and ORP;
 - b. Volatile organics;
 - c. Semi-volatile organics;
 - d. Temperature, pH, conductivity, DO, and ORP;
 - e. Total metals;
 - f. Dissolved metals;
 - g. Anions;
 - h. Temperature, pH, conductivity, DO, and ORP;
 - i. Radionuclides;
 - j. Alkalinity; and
 - k. Temperature, pH, conductivity, DO, and ORP.
- Measure the temperature, pH, conductivity, DO, and ORP on the first water extracted from the well. Take the measurements a total of 4 times during the evacuation process. Record the results, including the time of the measurement, on the Well Evacuation Summary sheet.
- Collect samples in the order specified in Section previously.
- Sample containers, preservative, maximum allowable holding times, and collection techniques are given in Sect. 5.5.
- Sample custody is to be maintained and documented by following standard operation procedure outlined in section A.6.
- Samples which require filtration will be filtered by using in-line, 0.45- μm filters. The filters can be obtained from QED Environmental Systems, Inc. The standard capacity filter (20-cm² surface area, catalog # FF-8100) should be used if the water can be filtered in a reasonable amount of time (i.e., 5 min/L). Use the Super filter I (600-cm² surface area, catalog # FF-9100) for more turbid samples.

5.6 Sample Containers, Preservatives, and Holding Times

Listed in Table 3 (Section 2 of report) are the sample containers, preservatives, and maximum allowable holding times for the groundwater samples to be used in this study. Sample containers are to be precleaned to EPA specifications. Samples for volatile and semivolatile organic compounds are to be collected with no headspace. In order to ensure that no headspace is present after capping, the sample container is to be inverted and gently tapped against the rubber-gloved hand of the person sampling. If air bubbles are observed, the sample is to be discarded and the bottle is to be filled with fresh formation water from the well. Samples will be collected in amber bottles in order to protect them from light. The dissolved metal sample must be filtered through a 0.45- μm filter prior to preservation with HNO_3 .

A.6. CHAIN-OF-CUSTODY REQUIREMENTS

A.6.1 Introduction

Ensuring the integrity of a sample from collection to data reporting is an essential part of any sampling and analyses plan. The documentation of sample history, referred to as chain of custody, includes the ability to trace the possession and handling of samples from the time of collection through analysis and final disposition.

Chain of custody is required for all compliance groundwater sampling and is necessary if there is any possibility that the analytical data or the conclusions based thereon will be used in litigation. The components of ORNL's chain of custody field log sheets, a chain of custody record, a sample analysis request sheet, and the procedures for their use are described in the following sections.

A.6.2 References

- Test Methods for Evaluating Solid Waste,
- DOE X-10 Plant Chain of Custody,
- Analytical Request Sheet,
- RCRA Groundwater Monitoring Technical Enforcement Guidance Document (TEGD), September 1986, OSWER9950.1.

A.6.3 Samples Under Custody

A sample is considered to be under a person's custody if one of these conditions is met:

- The sample is in a person's physical possession.
- The sample is in view of the person after he has taken possession.
- The sample is secured by that person so that no one can tamper with it.
- A sample is secured by a person in an area which is restricted to authorized personnel.

A.6.4 Chain-of-Custody Components

A.6.4.1 Sample Labels

Sample labels are necessary to prevent misidentification of samples. Labels should be completed and affixed to sample containers prior to or at the time of sampling. Paper or plastic labels with waterproof gummed backs or tags are appropriate; they must be written with blue or black waterproof ink and include the following information.

- Name(s) of collector(s);
- Date and time of collection;
- Sample identification (ID), which will identify the well, well location, and specific container;
- Parameter(s) requested, and
- Preservative(s).

6.4.2 Sample Seals

Sample seals are required for samples that are to be shipped or sent off-site (off the DOE reservation). Sample seals are used to detect unauthorized tampering of samples following sample collection up to the time of analysis. Gummed paper seals may be used for this purpose. The seal must be attached in such a way that it is necessary to break the seal in order to open the sample container. Seals must be affixed to containers before they leave the custody of sampling personnel. The seals should include the signature of the sampler or individual who seals the sample and the date the sample was sealed.

6.4.3 Field Log Sheets

All information pertinent to a field survey of sampling must be recorded on a log sheet. Sampling situations vary widely; therefore, no general rule can be given as to the extent of information that must be entered in the log book. A good rule, however, is to record sufficient information so that someone can reconstruct the sampling without reliance on the collector's memory. Keep the log sheets protected and in a safe place. Field log sheets to be used for groundwater sampling include the following:

- Immiscible Layer and Water Level Determination sheet,
- Immiscible Layer Sampling sheet,
- Well evacuation Summary sheet, and

- Sample Collection Summary sheet.

These forms are to be completed as described in the referenced Standard Operating Procedures. Fields should not be left blank. Fields should be marked NC (not collected) with an explanation provided under observations/deviation or NA (not applicable) if they do not apply.

Properly completed, these sheets along with the chain-of-custody sheet and Request for Analytical Services form discussed later in the section will provide the following information:

- Identification of well and well sample IDs;
- Well depth and method of determination (by measurement or well records);
- Static water level depth and measurement technique;
- Presence of immiscible layers and detection methods;
- Purge volume and pumping rates;
- Well purging initiation and completion times;
- Collection methods and sample IDs for immiscible layer samples;
- Well evacuation observations;
- Date, time and sequence of sample collection;
- Preservatives used;
- Field analyses and methods;
- Parameters requested for analysis;
- Field observations on purging and sampling of the wells;
- Climatic conditions at the time of sampling; and
- Name(s) of sample collector(s).

A.6.4.4 Chain-of-Custody Record

The chain-of-custody record must include the following:

- Sample ID,
- Signature(s) of collector(s),

- Date and time of collection, and
- Sample location.

A.6.5 Sample Submittal

Analyses will be conducted by the Analytical Chemistry Division (ACD) at ORNL. To avoid confusion and possible misplacement, each sample will be submitted directly to the laboratory responsible for making a given set of analyses. Form UCN-15840 (DOE X-10 Plant Chain of Custody) will be submitted with each sample.

- Samples for radiochemical analysis will be submitted to ACD at room F-50, Bldg. 4500 S. J. Wade will serve as a point of contact if there are any questions.
- Samples for cations will be submitted to ACD at room S159, Bldg. 4500 S. Joe Stewart will serve as a point of contact if there are any questions.
- Samples for anions will be submitted to ACD at room 210, Bldg. 1505. M. Ferguson will act as a point of contact.
- Samples for volatile and semi-volatile organics will be submitted to ACD at room F148, Bldg. 4500 S. John. Caton will act as a point of contact.

A.7. ALKALINITY

A.7.1 Introduction

Alkalinity is an important measurement for describing the major ion chemistry of groundwater. It is also essential for performing a charge balance as a check on the analytical precision of the cation and anion analysis for major ions present in the sample. Alkalinity can be moderately unstable especially when the groundwaters are under reducing condition. As a result, the alkalinity should be measured in the field whenever possible.

A.7.2 References

Techniques of Water-Resources Investigations of the United States Geological Survey, Chapter D2, Guideline for Collection and Field Analysis of Ground-Water Samples for Selected Unstable Constituents, W. W. Wood, 1976.

- Gran, G. (1952), Analyst 77, 661.
- Stumm, W. and Morgan, J. J. (1970) Aquatic Chemistry, Wesley-Interscience, New York, p. 144-146 and p 155-158.

A.7.3 Equipment and Materials

- Temperature-compensated pH meter and combination electrode.
- 25-mL buret with 0.1-mL graduations.
- Battery-powered magnetic stirrer with small Teflon-coated stirring bar.
- 25- and 50-mL class A volumetric pipets.
- 250-mL plastic squeeze bottle with nozzle for filling buret.
- 1-L of 0.01 N standard HCl. NOTE: 0.100 N (certified) HCl is available from stores (ORNL Stores # 03-001-1349), a 0.01 N solution can be made by making a volumetric 10X dilution.
- NBS pH buffers for pH = 7 and pH = 4.
- Clean and dry 150-mL beaker.

A.7.4 Procedure

- Standardize the pH meter and electrode with pH 7 and pH 4 NBS buffers.
- Pipet 50 mL of filtered sample into a clean, dry 150-mL beaker. Under no circumstances should the sample be diluted or concentrated in any way. The pipet should be rinsed three times with the sample water before final sample is placed in the beaker. If titration cannot be completed with one filling of the buret, discard sample and use a smaller sample size. There is a great chance for error in refilling a buret during a titration.
- Insert pH electrode into sample after it has been washed with distilled water and blotted, not wiped, dry. Insert clean dry stirring bar and adjust stirrer to slow speed.
- If pH is greater than 8.3, add HCl in approximately 0.1-mL increments, recording the volume added and the corresponding pH after each addition until the pH is below 8.0. When the pH of the sample during titration declines below 8.0, or the initial value is less than 8.3, add acid in increments of about 1 or 2 mL and record the pH at each increment. Continue this procedure until pH declines to approximately 5.5. From pH 5.5 to pH 4.0, add acid in approximately 0.1-mL increments. The most sensitive part of the titration is usually between pH 4.8 and 4.3. Continue to add acid past pH 4 in about 1-mL increments until the pH is approximately 3.0.

A.7.5 Calculations

One of the following methods will be used to calculate the total alkalinity:

A.7.5.1. Method A

A Gran plot is used in which a function F is defined as:

$$F = (V + V_0) (10^{-\text{pH}}),$$

where V_0 = original volume of sample, and
 V = volume of acid added.

The function F, evaluated for each titration point, is plotted as a function of the acid added (V). The linear part of the curve is extrapolated to $F = 0$, at which point $V = V_{\text{end}}$ point. The total alkalinity then equals $(C_t \times V_{\text{end}})/V_0$ where V_{end} is the volume of acid needed to reach the end point and C_t is the concentration of the acid in milliequivalents per liter (equal to the acid normality x 1000).

A.7.5.2. Method B

A plot of $\Delta\text{pH}/\Delta\text{mL}$ of titrant versus total titrant volume is made. The endpoint is determined as the value at which the maximum rate of change of pH per volume of titrant added occurs. The total alkalinity then equals $(C_t \times V_e)/V_o$, where V_e is the volume of acid needed to reach the end point and C_t is the concentration of the acid in milliequivalents per liter (equal to the acid normality $\times 1000$).

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