
Transuranic Chemical Species In Groundwater: Final Report

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February 1985

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TRANSURANIC CHEMICAL SPECIES
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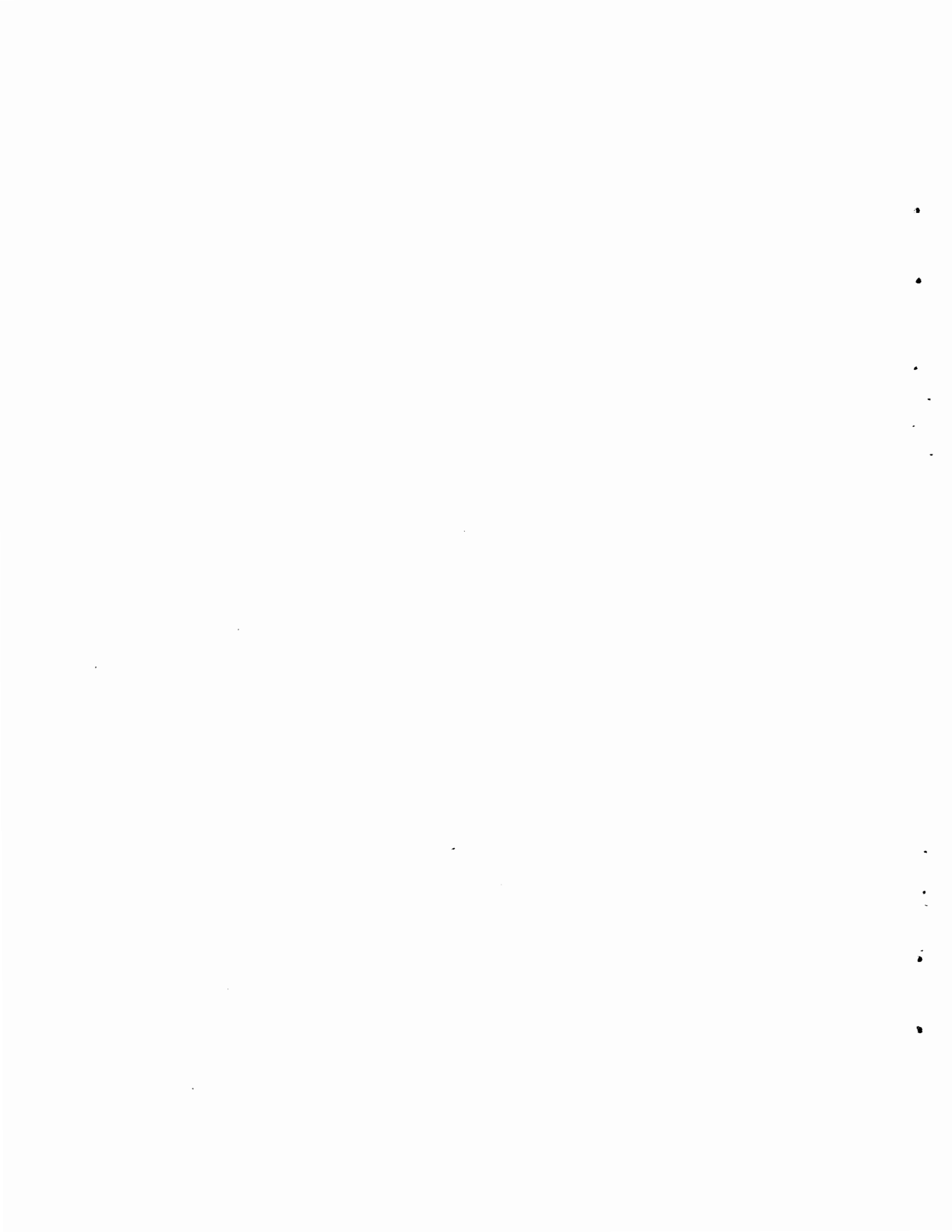
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SUMMARY

For the past several years, staff at Pacific Northwest Laboratory (PNL) have been studying the mobility of actinides, primarily plutonium, in the groundwater of a low-level disposal site. This research has provided valuable insights into the behavior of plutonium in the groundwater. Based on the analytical data and geochemical modeling, it appears that the plutonium that enters the trench, primarily in the higher oxidation states, Pu(V,VI), is rapidly reduced as the water migrates through the highly reducing sediments of the trench and is removed from the water by adsorption of the reduced plutonium, Pu(III,IV), onto the sediments. The Pu(V,VI) also appears to be reduced in the groundwater, although not as rapidly as in the trench sediments, and removed by adsorption. Because of the redox reduction that occurs during the migration of the groundwater, the system is not at redox equilibrium. Based on the discrepancies between the calculated and analytically determined redox distribution and charge-form speciation, the thermodynamic data bases for plutonium appear either to be missing or to contain incorrect thermodynamic data for several aqueous plutonium species, including the carbonate and organic complexes of plutonium. Further research is required to determine the kinetics of plutonium oxidation/reduction reactions in natural groundwater systems and to determine thermodynamic data for carbonate and organic complexes of plutonium.



CONTENTS

SUMMARY	iii
INTRODUCTION	1
DATA SOURCES AND METHODS	3
RESULTS	9
DISCUSSION	15
PLUTONIUM	15
Oxidation State	15
Charge Form Speciation	17
Organic Complexation	19
Particulate Concentration	22
Precipitation and Sorption	22
AMERICIUM	25
CONCLUSIONS AND RECOMMENDATIONS	27
REFERENCES	29
APPENDIX A - THERMODYNAMIC DATA FOR PLUTONIUM AQUEOUS SPECIATION	A.1
APPENDIX B - CHEMICAL COMPOSITION OF TRENCH, WELL AND SPRING WATERS FOR 1983	B.1
APPENDIX C - LOW-MOLECULAR-WEIGHT ORGANIC COMPOUNDS AND TOTAL DISSOLVED ORGANIC CARBON CONCENTRATIONS IN TRENCH, WELL AND SPRING WATERS FOR 1983	C.1
APPENDIX D - CALCULATED SATURATION INDICES FOR SELECTED SOLIDS	D.1

FIGURES

1	The Low-Level Radioactive Waste Disposal Facility and Locations of Sampling Points	3
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TABLES

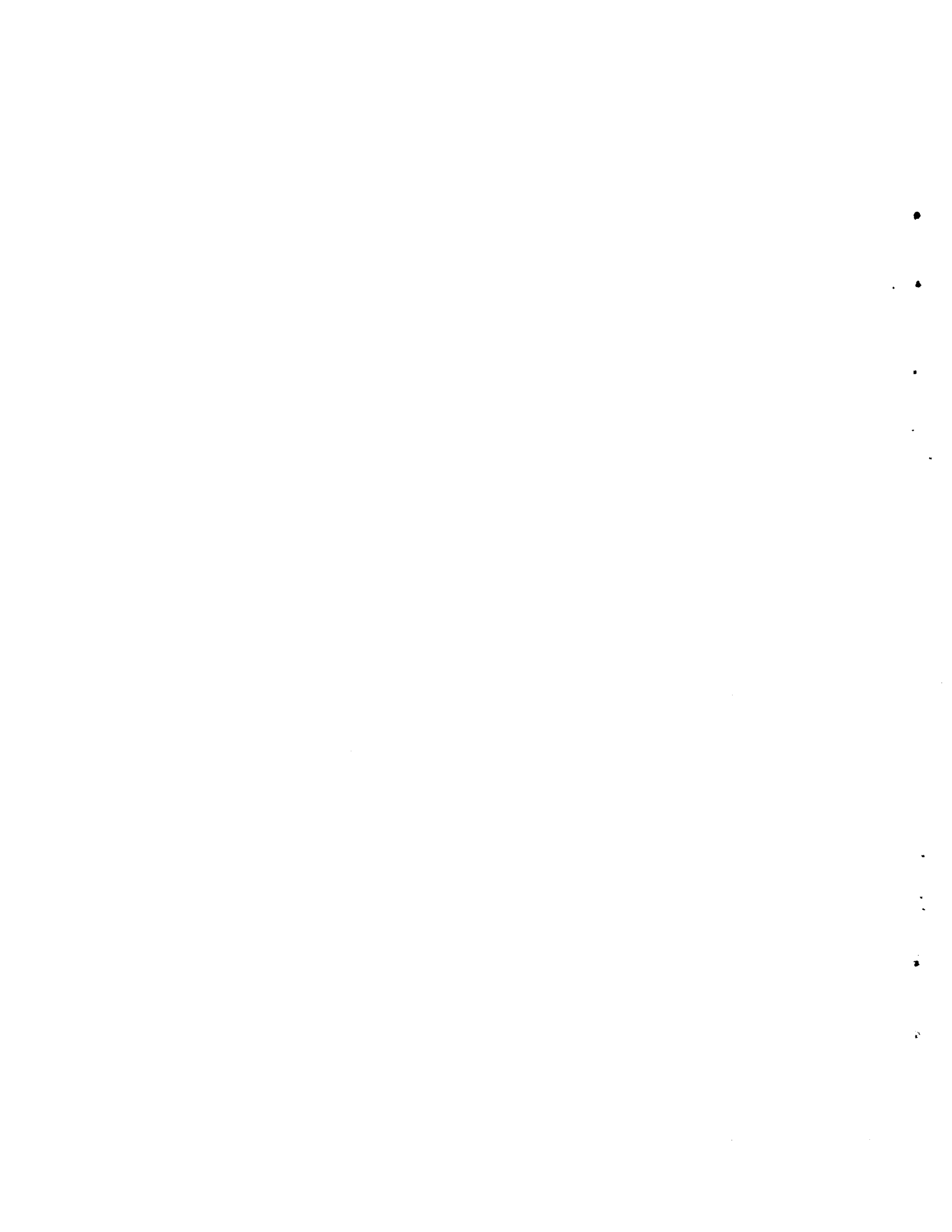
1	Chemical Reaction and Thermodynamic Data Used to Calculate Plutonium Aqueous Speciation	6
2	Stability Constants for Actinides with Citrate	7
3	Oxidation States and Concentrations of $^{239,240}\text{Pu}$ Determined at Pacific Northwest Laboratory	10
4	Concentrations of Plutonium and Americium Determined by Argonne National Laboratory	11
5	Aqueous Speciation of Plutonium Calculated Using Thermodynamic Data of Table 1	12
6	Aqueous Speciation of Plutonium Calculated Using Thermodynamic Data of Lemire and Tremaine (1980)	13

INTRODUCTION

The nuclear industry is faced with the challenging task of developing methods that are both feasible and environmentally sound for disposing of waters containing small amounts of radioactive contaminants. One method is to dispose of the contaminated waters in trenches where the radionuclides can be removed by precipitation or by adsorption on the sediments during infiltration and subsequent groundwater transport. However, it has been observed at some sites that certain radionuclides are quite mobile and are inadequately removed by adsorption on aquifer sediments (Means et al., 1978; Coles and Ramspott, 1982). In order to make this option feasible, therefore, the processes that contribute to the mobility and retardation of the radionuclides need to be identified and their effects quantified.

For the past several years, staff at Pacific Northwest Laboratory (PNL) have been studying radionuclide mobility in the groundwater of a low-level disposal site. This report summarizes and interprets the results obtained to date on actinides, primarily plutonium, in that system. It constitutes a final report for the project, which was terminated at the end of FY83. A companion project, funded by the U.S. Nuclear Regulatory Commission (NRC), has examined the mobility of other radionuclides at this site. The results from that project are summarized in the annual reports to NRC (Robertson et al., 1981, 1983; Fruchter et al., 1984).

The overall objective of this research project was to identify and evaluate, as possible, the processes controlling the mobility of plutonium at this site, with the ultimate goal of increasing our understanding of the factors affecting the mobility of plutonium in groundwaters. In this final report, the available data are presented and interpreted and areas for future research identified.



DATA SOURCES AND METHODS

The low-level disposal site consists of an unlined basin and a connecting trench that receive influent water containing low levels of fission and activation products and trace amounts of transuranic radionuclides (Figure 1). The influent water percolates through the sediment, and a small fraction of it emerges at seepage springs approximately 260 meters down slope. Prior to January 1983, influent water samples were collected from a sampling line that tapped the influent water flow just before it entered the disposal facility. In 1983, influent water was sampled at the inlet (manway #1 or #2) and the far end of the trench (manway #10). The bottom of the trench is unlined and the top is presently covered with prestressed concrete slabs containing manways for access to the trench. Because the seepage springs were often inaccessible, the water was sampled

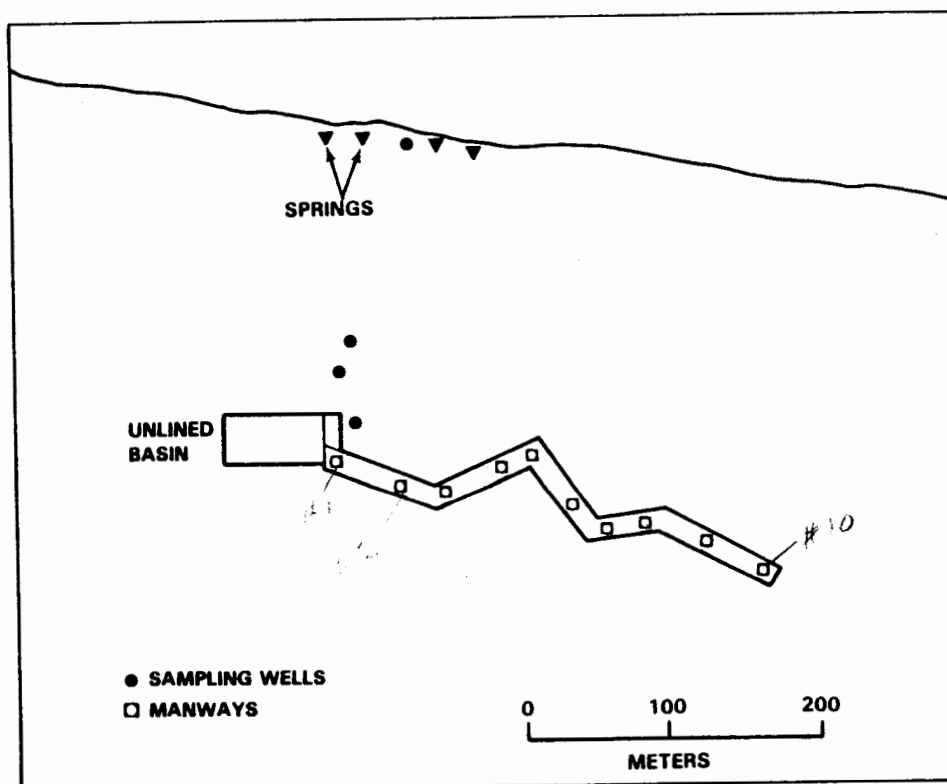


FIGURE 1. The Low-Level Radioactive Waste Disposal Facility and Locations of Sampling Points

from a well placed upgradient of the seepage springs. Three sampling wells were installed in 1982, at distances of 30, 46, and 73 meters from the trench, to permit sampling of the groundwater between the trench and the seepage springs (Robertson et al., 1983). Well #1 at 30 meters and Well #3 at 73 meters were used for sampling. Well #2 at 46 meters was not sampled because it had a bent casing that could not accommodate the sampling pump. All water samples were collected approximately one meter below the water surface.

The analytical techniques used at PNL to determine the total plutonium concentration and plutonium oxidation state are described in Robertson and Abel (1980, 1981). For each sample, the oxidation state and concentration were determined on two aliquots of water. The analytical techniques for oxidation state determination (Lovett and Nelson, 1981) can only distinguish between the reduced forms, Pu(III) and Pu(IV), and the oxygenated forms, Pu(V) and Pu(VI). The cationic, anionic, and nonionic charge form speciation and particulate distribution were determined on one sampling date (September 1981) using the Battelle large volume water sampler (Silker, Perkins and Rieck, 1971; Silker, 1975).

In 1983, several samples of the influent and groundwater were analyzed at Argonne National Laboratory for concentrations of total, dissolved and particulate plutonium, the plutonium oxidation states [i.e., Pu(III,IV) versus Pu(V,VI)] and the total dissolved and particulate concentrations of americium. The analysis techniques for total, dissolved and particulate plutonium are similar to those reported by Robertson and Abel (1980, 1981). The plutonium oxidation state was determined using the procedure of Lovett and Nelson (1981). Americium and plutonium were removed from the solution by iron scavenging followed by anion exchange purification steps. Americium was determined using the cation exchange procedure of Kanab (1979).

At the same time that water samples were taken for radionuclide analysis, samples were collected for detailed measurements of dissolved organic carbon (DOC), major cations and anions, trace elements and dissolved organic constituents. Temperature, pH, Eh, dissolved oxygen and alkalinity were measured onsite as the samples were collected. Aliquots of

0.4-micron filtered water were frozen for later laboratory analysis of major anions by ion chromatography. For major cation and trace element analysis, a separate aliquot of filtered water was acidified by adding 20 mL of concentrated Ultrex(T) hydrochloric acid per liter of water. For the sulfide analysis, an inline filtered sample of water was collected in a glass bottle containing an antioxidant buffer and analyzed by a sensitive polarographic technique. Another aliquot of water was collected and preserved by filtration and refrigeration for dissolved organic carbon constituent analysis. Details of the analytical techniques are presented in Fruchter et al. (1984).

The aqueous species distribution for plutonium was calculated using the MINTEQ geochemical model (Felmy, Girvin and Jenne, 1984). The thermodynamic data were taken either from a recent plutonium thermodynamic data review (Table 1; also Appendix A) or from the thermodynamic data compilation of Lemire and Tremaine (1980). Both thermodynamic data bases were used because of the current uncertainties in the thermodynamic data for plutonium. The activities of the aqueous species and the saturation indices for solid phases were calculated from the total dissolved plutonium concentration (converted to mg L^{-1}), the concentration of other constituents in the water, and the pH, Eh and temperature of the water.

A significant portion of the dissolved plutonium may be complexed by natural and synthetic ligands present in the infiltrating water. We lacked detailed data (organic compounds present and the stability constants for their reaction with plutonium) necessary to permit speciation calculation; therefore, we made a rough estimate of the extent of organic complexation of Pu(V,VI) by using estimated $\log K_r$ values for the Pu(V,VI)-organic complexes. Citrate was the only organic ligand that was identified and quantified in the waters. The stability constants for Pu(V)-citrate complexes were estimated as the average of the tabulated values of the stability constants for the 1:1 and the 1:2 complexes of citrate with other actinides (Table 2). No stability constants were found in the literature for the reaction of plutonium with fulvic and humic acids. For these waters, therefore, the conditional stability constant for iron (Fe^{3+}) complexation with humic acid was used to estimate the stability constant for the complexation of PuO_2^{2+} and PuO_2^+ with fulvic and humic acids.

TABLE 1. Chemical Reaction and Thermodynamic Data Used to Calculate Plutonium Aqueous Speciation^(a)

Reaction	Log K_r°
$\text{Pu}^{4+} + \text{H}_2\text{O} = \text{PuOH}^{3+} + \text{H}^+$	0.11
$\text{Pu}^{4+} + 2\text{H}_2\text{O} = \text{Pu}(\text{OH})_2^{2+} + 2\text{H}^+$	-0.18
$\text{Pu}^{4+} + 3\text{H}_2\text{O} = \text{Pu}(\text{OH})_3^+ + 3\text{H}^+$	-3.28
$\text{Pu}^{4+} + 4\text{H}_2\text{O} = \text{Pu}(\text{OH})_4^{\circ} + 4\text{H}^+$	-9.48
$2\text{PuO}_2^{2+} + 2\text{H}_2\text{O} = (\text{PuO}_2)_2(\text{OH})_2^{2+} + 2\text{H}^+$	-8.2
$4\text{PuO}_2^{2+} + 7\text{H}_2\text{O} = (\text{PuO}_2)_4(\text{OH})_7^+ + 7\text{H}^+$	-29.11
$\text{Pu}^{3+} + \text{SO}_4^{2-} = \text{PuSO}_4^+$	3.614
$\text{Pu}^{3+} + 2\text{SO}_4^{2-} = \text{Pu}(\text{SO}_4)_2^-$	5.470
$\text{Pu}^{4+} + \text{SO}_4^{2-} = \text{PuSO}_4^{2+}$	4.819
$\text{Pu}^{4+} + \text{SO}_4^{2-} = \text{Pu}(\text{SO}_4)_2^{\circ}$	8.709
$\text{PuO}_2^{2+} + \text{SO}_4^{2-} = \text{PuO}_2\text{SO}_4^{\circ}$	3.374
$\text{Pu}^{3+} + \text{NO}_3^- = \text{PuNO}_3^{2+}$	1.41
$\text{Pu}^{3+} + 2\text{NO}_3^- = \text{Pu}(\text{NO}_3)_2^+$	2.22
$\text{Pu}^{3+} + 3\text{NO}_3^- = \text{Pu}(\text{NO}_3)_3^{\circ}$	2.52
$\text{Pu}^{4+} + \text{NO}_3^- = \text{PuNO}_3^{3+}$	0.54
$\text{Pu}^{4+} + 2\text{NO}_3^- = \text{Pu}(\text{NO}_3)_2^{2+}$	1.00
$\text{PuO}_2^{2+} + \text{NO}_3^- = \text{PuO}_2\text{NO}_3^+$	-1.14
$\text{Pu}^{3+} + \text{Cl}^- = \text{PuCl}^{2+}$	-1.187
$\text{Pu}^{4+} + \text{Cl}^- = \text{PuCl}^{3+}$	0.094
$\text{Pu}^{4+} + 2\text{Cl}^- = \text{PuCl}_2^{2+}$	-0.74
$\text{PuO}_2^{2+} + \text{Cl}^- = \text{PuO}_2\text{Cl}^+$	0.068
$\text{PuO}_2^{2+} + 2\text{Cl}^- = \text{PuO}_2\text{Cl}_2^{\circ}$	-2.07
$\text{Pu}^{4+} + \text{F}^- = \text{PuF}^{3+}$	7.567
$\text{Pu}^{4+} + 2\text{F}^- = \text{PuF}_2^{2+}$	13.687
$\text{PuO}_2^{2+} + \text{F}^- = \text{PuO}_2\text{F}^+$	4.0337
$\text{Pu}^{4+} + 4\text{H}_2\text{O} + \text{CO}_3^{2-} = \text{Pu}(\text{OH})_4\text{CO}_3^{2-} + 4\text{H}^+$	-3.48
$\text{Pu}^{4+} + 2\text{H}^+ + \text{PO}_4^{3-} = \text{Pu}(\text{H}_2\text{PO}_4)^{3+}$	24.49
$\text{Pu}^{4+} + 4\text{H}^+ + 2\text{PO}_4^{3-} = \text{Pu}(\text{H}_2\text{PO}_4)_2^{2+}$	47.43
$\text{Pu}^{4+} + 8\text{H}^+ + 4\text{PO}_4^{3-} = \text{Pu}(\text{H}_2\text{PO}_4)_4^{\circ}$	92.12
$\text{Pu}^{3+} + 2\text{H}^+ + \text{PO}_4^{3-} = \text{PuH}_2\text{PO}_4^{2+}$	21.643
$\text{Pu}^{3+} + 4\text{H}^+ + 2\text{PO}_4^{3-} = \text{Pu}(\text{H}_2\text{PO}_4)_2^+$	42.306
$\text{Pu}^{4+} + 2\text{H}_2\text{O} = \text{PuO}_2^+ + \text{e}^- + 4\text{H}^+$	-18.6
$\text{Pu}^{3+} + 2\text{H}_2\text{O} = \text{PuO}_2^+ + 2\text{e}^- + 4\text{H}^+$	-35.5
$\text{PuO}_2^{2+} + \text{e}^- = \text{PuO}_2^+$	16.3

(a) See Appendix A for sources of data.

TABLE 2. Stability Constants for Actinides with Citrate
(from Martell and Smith, 1977)

<u>Actinide</u>	<u>Reaction</u>	<u>Log K_r</u>	<u>Conditions</u>	<u>Log K_r^o</u>
Am ³⁺	Am ³⁺ + citrate ³⁻ = Am - citrate ^o	7.74	25°, 0.1	9.67
	Am ³⁺ + 2citrate ³⁻ = Am - 2citrate ³⁻	10.9	25°, 0.1	12.82
UO ₂ ²⁺	UO ₂ ²⁺ + citrate ³⁻ = UO ₂ - citrate ⁻	7.4	25°, 0.1	8.90
Cm ³⁺	Cm ³⁺ + citrate ³⁻ = Cm - citrate ^o	7.74	25°, 0.1	9.67
	Cm ³⁺ + 2citrate ³⁻ = Cm - 2citrate ³⁻	10.9	25°, 0.1	12.82



RESULTS

The plutonium and americium concentrations in the influent and groundwaters are given in Tables 3 and 4. The physical and chemical measurements of the influent and groundwaters in 1983 are presented in Appendix B. The measurements of the dissolved organic concentration of selected samples in 1983 and the constituents in the low-molecular-weight fraction in these samples are presented in Appendix C. The dissolved organic carbon concentrations range from <1 to approximately 19 mg L⁻¹. In the influent water sample from September 1981, the major organic compound in the low-molecular-weight fraction was identified as citrate (0.38 mg L⁻¹), a chemical commonly used in decontamination solutions (Robertson et al., 1981).

Tables 5 and 6 present a summary of the plutonium speciation calculations using the two thermodynamic data bases and the physical and chemical characteristics of the water samples.

All plutonium solid phases presently in the MINTEQ data base were calculated to be undersaturated by at least three orders of magnitude. The following solid phases were included in the saturation index calculations: Pu(OH)_{2.5}Cl_{0.5}, Pu(OH)₃, β-PuO₃, PuO₂(c), PuO₂(lc), Pu(OH)₄(a), PuO₂(OH), Pu(HPO₄)₂, PuF₃, PuF₄, and Pu(SO₄)₂. The saturation indices were calculated assuming the measured distribution of plutonium between the lower (III and IV) and higher (V and VI) oxidation states. The saturation indices for other selected solid phases are presented in Appendix D.

TABLE 3. Oxidation States and Concentrations of $^{239,240}\text{Pu}$
Determined at Pacific Northwest Laboratory

<u>Location</u>	<u>Date</u>	<u>Pu(III + IV) fCi/L (%)</u>	<u>Pu(V + VI) fCi/L (%)</u>	<u>Total fCi/L</u>
Influent	3/3/81	(8-10)	(90-92)	54,200 to 57,700
	6/17/81	(8-9)	(91-92)	23,600 to 28,500
Trench				
First Manway	2/15/83	19,000 (8)	220,000 (92)	240,000
* Last Manway	2/15/83	24,000 (23)	81,000 (77)	110,000
Well #1	2/15/83	550 (71)	220 (29)	780
Well #3	2/17/83	170 (61)	110 (39)	280
Springs				
	10/24/79	(11-20)	(80-89)	102 to 22
	3/3/81	(11-13)	(87-89)	10 to 7.9
	6/17/81	(3-14)	(86-96)	300 to 44
	2/17/83	28 (36)	49 (64)	77

TABLE 4. Concentrations of Plutonium and Americium Determined by Argonne National Laboratory

Sample Form	Date	Pu(III,IV)	Pu(V,VI)	Total Pu(III,IV) + Pu(V,VI) ^(a)		Dissolved Pu Total ^(b)	Pu Particulate		Dissolved Am	Particulate Am
		fCi/L	fCi/L	fCi/L	%	fCi/L	%	fCi/L		
1st Manway	2/15/83	30,800	128,800	159,600	81	--	--	14,200	--	
1st Manway	3/30/83	11,000	89,000	100,000	89	100,000	45,000	31	5,100	30,000
2nd Manway	5/5/83	17,300	1,900	19,200	10	17,400	64,000	79	7,900	50,000
2nd Manway	6/16/83	13,100	19,100	32,200	59	25,000	22,000	47	9,400	11,000
Last Manway	2/15/83	38,200	119,800	158,000	76	--	--	--	13,700	--
	3/30/83	20,000	71,000	91,000	78	85,300	23,000	21	9,900	13,400
	5/5/83	15,000	1,100	16,100	7	13,900	83,000	86	4,900	56,000
	6/16/83	10,700	18,300	29,000	63	23,000	--	--	10,000	--
Well #1	2/15/83	21.4	8.0	29.4	27	--	0.11	--	--	0.06
	3/31/83	41.0	84.0	125	67	72.6	0.31	0.4	23.0	1.60
	5/6/83	-- ^(c)	--	--	--	--	0.20	--	--	0.07
Well #3	2/17/83	0.46	0.59	1.05	56	--	0.05	--	0.53	0.03
Spring	2/17/83	0.86	1.54	2.40	64	--	0.02	7	0.83	0.01
	4/1/83	4.5	14.8	19.3	77	10.1	0.08	0.8	1.45	0.42
	5/9/83	0.86	3.07	3.93	78	1.26	0.46	26.7	0.70	0.37
	6/20/83	0.87	1.18	2.05	58	1.36	0.0	--	0.76	2.4
	9/12/83	0.70	1.47	2.17	68	2.03	0.12	5.6	0.66	0.06

(a) Determined by addition of previous two columns and represents total dissolved Pu.

(b) Determined by evaporation and analysis.

(c) -- Sample not analyzed.

TABLE 5. Aqueous Speciation of Plutonium Calculated Using Thermodynamic Data of Table 1

Sampling Location	Sampling Date	Pu(III,IV) (%)	Pu(V,VI) (%)	Dominant Species and Percentage
Influent	3/10/81	>99	<1	$\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ (58.2) $\text{Pu}(\text{OH})_4^0$ (39.5) $\text{Pu}(\text{OH})_3^+$ (2.3)
	6/17/81	>99	<1	$\text{Pu}(\text{OH})_4^0$ (58.9) $\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ (21.6) $\text{Pu}(\text{OH})_3^+$ (19.6)
1st Manway	2/15/83	>99	<1	$\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ (99.2)
	3/30/83	>99	<1	$\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ (96.1) $\text{Pu}(\text{OH})_4^0$ (3.9)
2nd Manway	5/5/83	>99	<1	$\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ (98.8) $\text{Pu}(\text{OH})_4^0$ (1.2)
	6/16/83	>99	<1	$\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ (51.2) $\text{Pu}(\text{OH})_4^0$ (45.0) $\text{Pu}(\text{OH})_3^+$ (3.8)
Last Manway	2/15/83	>99	<1	$\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ (99.2)
	3/30/83	>99	<1	$\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ (97.0) $\text{Pu}(\text{OH})_4^0$ (3.0)
	5/5/83	>99	<1	$\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ (97.3) $\text{Pu}(\text{OH})_4^0$ (2.7)
	6/16/83	>99	<1	$\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ (47.7) $\text{Pu}(\text{OH})_4^0$ (47.3) $\text{Pu}(\text{OH})_3^+$ (5.0)
Well #1	2/15/83	>99	<1	$\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ (92.9) $\text{Pu}(\text{OH})_4^0$ (7.1)
	3/31/83	>99	<1	$\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ (93.8) $\text{Pu}(\text{OH})_4^0$ (6.2)
Well #3	2/17/83	>99	<1	$\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ (95.3) $\text{Pu}(\text{OH})_4^0$ (4.7)
Spring	3/3/81	>99	<1	$\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ (85.5) $\text{Pu}(\text{OH})_4^0$ (14.2)
	6/17/81	>99	<1	$\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ (90.5) $\text{Pu}(\text{OH})_4^0$ (9.3)
	2/17/83	>99	<1	$\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ (92.1) $\text{Pu}(\text{OH})_4^0$ (7.8)
	4/1/83	>99	<1	$\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ (92.0) $\text{Pu}(\text{OH})_4^0$ (7.9)
	5/9/83	>99	<1	$\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ (85.7) $\text{Pu}(\text{OH})_4^0$ (14.3)
	6/20/83	>99	<1	$\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ (89.1) $\text{Pu}(\text{OH})_4^0$ (10.7)
	9/12/83	>99	<1	$\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ (92.1) $\text{Pu}(\text{OH})_4^0$ (7.8)

TABLE 6. Aqueous Speciation of Plutonium Calculated Using Thermodynamic Data of Lemire and Tremaine (1980)

Sampling Location	Sampling Date	Pu(III,IV) (%)	Pu(V,VI) (%)	Dominant Species and Percentage
Influent	3/10/81	>99	<1	$\text{Pu}(\text{OH})_5^-$ (95.4) $\text{Pu}(\text{OH})_4^0$ (4.6)
	6/17/81	>99	<1	$\text{Pu}(\text{OH})_5^-$ (81.3) $\text{Pu}(\text{OH})_4^0$ (18.7)
1st Manway	2/15/83	>99	<1	$\text{Pu}(\text{OH})_5^-$ (99.9)
	3/30/83	>99	<1	$\text{Pu}(\text{OH})_5^-$ (99.7)
2nd Manway	5/5/83	>99	<1	$\text{Pu}(\text{OH})_5^-$ (99.9)
	6/16/83	>99	<1	$\text{Pu}(\text{HPO}_4)_4^{4-}$ (66.5) $\text{Pu}(\text{OH})_5^-$ (31.7) $\text{Pu}(\text{OH})_4^0$ (1.8)
Last Manway	2/15/83	>99	<1	$\text{Pu}(\text{OH})_5^-$ (99.9)
	3/30/83	>99	<1	$\text{Pu}(\text{OH})_5^-$ (99.8)
	5/5/83	>99	<1	$\text{Pu}(\text{OH})_5^-$ (99.8)
	6/16/83	>99	<1	$\text{Pu}(\text{HPO}_4)_4^{4-}$ (92.1) $\text{Pu}(\text{OH})_5^-$ (7.4)
Well #1	2/15/83	>99	<1	$\text{Pu}(\text{OH})_5^-$ (99.1)
	3/31/83	>99	<1	$\text{Pu}(\text{OH})_5^-$ (99.4)
Well #3	2/17/83	>99	<1	$\text{Pu}(\text{OH})_5^-$ (99.0)
Spring	3/3/81	>99	<1	$\text{Pu}(\text{OH})_5^-$ (98.6) $\text{Pu}(\text{OH})_4^0$ (1.4)
	6/17/81	>99	<1	$\text{Pu}(\text{OH})_5^-$ (99.1)
	2/17/83	>99	<1	$\text{Pu}(\text{OH})_5^-$ (99.0)
	4/1/83	>99	<1	$\text{Pu}(\text{OH})_5^-$ (99.2)
	5/9/83	>99	<1	$\text{Pu}(\text{OH})_5^-$ (98.7) $\text{Pu}(\text{OH})_4^0$ (1.3)
	6/20/83	>99	<1	$\text{Pu}(\text{OH})_5^-$ (98.8) $\text{Pu}(\text{OH})_4^0$ (1.2)
	9/12/83	>99	<1	$\text{Pu}(\text{OH})_5^-$ (99.2)



DISCUSSION

The distribution of any element in a given water body is determined by equilibrium among the complexation, adsorption, oxidation/reduction and precipitation/dissolution reactions. If all these reactions achieve equilibrium rapidly, then the aqueous speciation and aqueous-solid phase partitioning of an element can be calculated using an equilibrium model. If, however, one or more of these processes significantly depart from equilibrium, then discrepancies between the calculated and analytical values will result.

PLUTONIUM

Plutonium has been measured in the groundwaters of the site in femtocurie per liter concentrations (Tables 3 and 4). The determinations made at Pacific Northwest Laboratory (PNL) and Argonne National Laboratory (ANL) differ significantly even for the one sampling date (February 1984) when duplicate samples were analyzed at the two laboratories. The concentrations determined at ANL are lower than those determined at PNL. Generally, when the accuracy of radionuclide analysis is evaluated, the lower value is considered most accurate because of the potential for contamination especially when measurements are made of femtocurie concentrations. However, the proportions of plutonium in the lower and higher oxidation states are similar between the two laboratories, suggesting that if contamination did occur it did not significantly affect the plutonium distribution.

Oxidation State

The oxidation state of the plutonium strongly influences the type of complexes formed, the strength of adsorption (Strickert, 1980), and the biological availability (Nelson, Kennedy and Conway, 1979). Plutonium is the only chemical element for which four oxidation states can coexist at equilibrium in aqueous solution. The analytical data indicate that the Pu(V,VI) oxidation states are dominant in both the influent and groundwaters (Tables 3 and 4). There are lesser, but significant, amounts of

plutonium in the Pu(III,IV) oxidation states. The aqueous speciation calculations using both thermodynamic data bases (Tables 5 and 6), however, indicate that if the plutonium is assumed to be in equilibrium with the measured Eh, the dominant oxidation state is IV. The discrepancy between the analytical and the calculated dominant oxidation states suggests that these waters are not in redox equilibria or that the analytical measurements are in error.

Since redox sensitive elements are generally in thermodynamic disequilibria in surface and groundwaters (Jenne et al., 1980; Jenne, 1981; Lindberg and Runnells, 1984), disequilibria of plutonium with the couples sensed by the platinum electrode is also very likely. Lindberg and Runnells (1984) observed that multiple redox couples present in individual samples yielded computed Eh values that did not agree with each other nor with the Eh measured in the field with a platinum electrode. On the other hand, laboratory experiments using samples of the groundwater spiked with plutonium either in the lower or higher oxidation states in contact with Lake Michigan sediment rapidly attained an oxidation state distribution similar to that measured at the site (D. M. Nelson, personal communication, 1984). Measurements of the oxidation state of plutonium in natural waters (Wahlgren et al., 1979; Wahlgren and Orlandini, 1982) indicate that in oxygenated waters low in organic carbon similar to those at this site, the higher oxidation states of plutonium dominate. These results suggest that the plutonium has attained some sort of steady state distribution in the groundwater and also that the discrepancy between the analytical and calculated redox distribution could be due to incomplete thermodynamic data for aqueous plutonium complexes. For example it is possible that the thermodynamic data to represent the redox couples, especially that between Pu(IV) and Pu(V), are incorrect. The thermodynamic data for the redox couples are nearly identical for the two data bases and virtually identical to the redox couple data accepted by Rai and Serne (1978) and Allard, Olofsson and Tortenfelt (1984). This agreement is most likely due to the acceptance of the thermodynamic data of Fuger and Oetting (1976) by all four compilations. An increase in the number and strength of Pu(V) and Pu(VI) complexes and/or a decrease in the number and strength of Pu(IV) complexes would result in a shift in the calculated distribution toward the

higher oxidation states. Silver (1983), assuming that only carbonate species of Pu(IV) and Pu(VI) are important, demonstrated that a slight change in the Pu(IV)-carbonate stability constant would result in a shift in the redox distribution toward a dominance of Pu(V) instead of Pu(IV).

One possible explanation for the observed discrepancy is an analytical error in the Eh estimates. However, even if the Eh values are increased by 300 to 400 mV, the Pu(V,VI) oxidation states account for only approximately one-third of the total dissolved plutonium.

Plutonium enters the system predominantly in the higher oxidation states, and reduction to the lower oxidation states appears to be occurring in the groundwater. On a given sampling date, the percentage of the total dissolved plutonium in the higher oxidation states is significantly lower ($p < 0.05$) at the seepage springs than at the trench. These results suggest that in future studies at other sites the plutonium oxidation state will need to be evaluated analytically, because of the potential for redox disequilibria, in order to predict reliably the mobility of the plutonium.

Charge Form Speciation

In September 1981, D. E. Robertson and K. H. Abel measured the charge form of the plutonium in the groundwater by adsorption onto resin beds (Pacific Northwest Laboratory, unpublished data) and determined that nearly all (>90%) of the migrating plutonium is in the anionic charge form. If the waters are assumed to be in equilibrium with the measured Eh, then the dominant charge form from both sets of the thermodynamic data is anionic (see Table 5). However, given the redox disequilibria for plutonium, this is unlikely to be the actual species distribution in these waters. If it is assumed that only the higher oxidation states occur in the water, then the dominant oxidation state, based on the thermodynamic data in Table 1, would be Pu(V), and the dominant species PuO_2^+ . Consequently, the dominant charge form would be cationic, which disagrees with the analytical measurements. The dominant charge form measured in the Great Lakes, which are similar to the waters at this site, was anionic (Conway et al., 1977) in agreement with the analytical measurements at this site.

One explanation for this discrepancy between the measured charge form speciation and that predicted by the geochemical model is the absence of carbonate complexes for the higher oxidation states from the thermodynamic data base. A previous thermodynamic assessment of plutonium speciation (Rai and Serne, 1978) suggested that under the water conditions prevalent at the crib and seepage springs, the dominant plutonium species would be the anionic $\text{PuO}_2\text{CO}_3\text{OH}$ -complex. The unpublished thermodynamic data review by Schwab and Felmy concluded that the reported thermodynamic data for carbonate complexes of plutonium were inconsistent with the available experimental measurements and, therefore, were not included in their thermodynamic data base. Since the results of this review are presented in Table 1, carbonate complexes for the higher oxidation states are not considered. Lemire and Tremaine (1980) do include thermodynamic data for the anionic complex, $\text{PuO}_2(\text{CO}_3)_2^{2-}$, in their compilation. If the thermodynamic data of Lemire and Tremaine (1980) are used and it is assumed that all the plutonium is in the higher oxidation states, this anionic carbonate complex is calculated to be the dominant Pu(VI) species. However, the calculated speciation indicates that the dominant oxidation state for these waters is Pu(V) and the dominant species to be PuO_2^+ . Thus, this thermodynamic data base would also predict that the dominant charge form is cationic. The presence of carbonate complexes, especially of Pu(V) and Pu(VI), and their importance need to be evaluated further, not just to resolve the discrepancy between the charge form distributions but also to resolve the discrepancy between the calculated and analytical redox distributions.

Although discrepancies between the analytical and calculated charge form distributions could be due to inaccurate or incomplete thermodynamic data for some of the plutonium aqueous species, another possible explanation is that the plutonium on the anion resin is altered by reaction with the resins. For example, Don Nelson (personal communication, 1984) found that when the adsorbed plutonium, which was predominantly in the Pu(V,VI) oxidation states, was removed from the anion resin, it was all in the Pu(III,IV) oxidation states. These results suggest that the resin is reducing the plutonium and altering the species distribution. Since the dominant species of the lower oxidation states as noted above are anionic,

then this could account for the anionic species. Another possible explanation is that the release of H^+ ions from the H^+ cation resin would lower the pH and could alter the speciation resulting in a predominance of the anionic charge form. However, at a lower pH the predominant species would still be cationic.

Organic Complexation

Another possible reason for the discrepancy between the dominant charge form calculated from both sets of thermodynamic data and the analytical measurement could be the formation of an anionic complex of Pu(V,VI) with organic ligands present in the water. The total dissolved organic carbon concentration in the crib and spring waters range from less than 1 to approximately 19 mg L^{-1} . The bulk of the organic carbon content of the waters (>98%) is composed of relatively non-volatile compounds, of high molecular weight (MW), that are not detected using GC analysis. The relative abundance of these compounds as compared to the low-MW organic acids suggests that the high-MW compounds will prove to be important in mobilizing radionuclides. Research has indicated that these high-MW organic compounds can be important in binding radionuclides (Carlsen, Bo and Larsen, 1984; Means, Crerar and Duguid, 1978) especially since significant quantities of low-MW chelating agents were not identified in these waters with the exception of citrate on a single sampling date. Large quantities (ppm levels) of synthetic chelating agents such as EDTA, HEDTA and ED3A have been identified at other low-level disposal sites (Means, Crerar and Duguid, 1978; Rees and Cleveland, 1982; Toste et al., 1983; Toste, Kirby and Pahl, 1984) and appear to be responsible for the observed mobility of radionuclides, including plutonium, at these sites.

In the one influent water sample analyzed (September 1981), the major low-MW dissolved organic compounds identified in the crib waters were citrate and oxalate, which are used as decontaminants in nuclear power plants; silicone oils, which are used in lubrication; and palmitic and stearic acids, which are used in soaps and detergents as well as being natural decontamination products of bioorganic matter. Citrate forms strong complexes with a number of transition metals (Martell and Smith,

1977); hence, it is potentially important in plutonium speciation, especially in view of its elevated concentration.

Numerous carboxylic acids were identified in the trench waters, generally at ppb levels, but elevated concentrations of either citrate or oxalate were not detected in the 1983 samples of the trench waters. Four classes of carboxylic acids were identified: dicarboxylic acids, monocarboxylic acids, oxygenated acids, and aromatic acids. The monocarboxylic and dicarboxylic acids are common bio-organic compounds, and the oxygenated and aromatic acids are typical products of microbial activity. In general, the concentration of the low-MW acids decreased along the trench. The trench was the site of substantial algal blooms before the cement cover was placed over it. Some of the organic acids may have originated from the decay of this organic matter.

The major low-MW dissolved organic compounds in the spring and groundwaters are the long-chained monocarboxylic acids. These acids are formed naturally during the decomposition of natural organic matter. The oxygenated acids are absent in the groundwater, and the dicarboxylic and aromatic acid concentrations are less than those measured in the trench. The low-MW organic acids in the seepage spring and ground waters constitute only 0.05 to 0.19 percent of the total dissolved organic carbon. In the September 1981 sample of the seepage spring water, the citrate concentration was quite low compared to the concentration entering the crib. One possible explanation for the large decrease in the citrate concentration is that the citrate measured from the one grab sample of water entering the crib was a spike and did not represent average conditions. Alternative explanations are that the citrate was adsorbed onto the bed sediments, since high concentrations of citrate have been detected in the trench sediments (Robertson et al., 1983), or that the citrate was degraded by micro-organisms.

Some researchers have suggested that the anionic and neutral charge forms of plutonium found in many natural waters are organic complexes and not carbonate complexes (e.g., Sholkovitz, 1983). For example, waters of low pH (3.9 to 5.3), where carbonate complexes would be insignificant, and

high dissolved organic carbon content had a very high percentage of the dissolved plutonium associated with uncharged forms (Alberts et al., 1977). Wahlgren, Chase and Alberts (1979) concluded that organic ligands form stronger complexes with Pu(IV) than Pu(VI). These findings are supported by the observed decrease in the Pu(VI)/Pu(IV) ratio from oligotrophic to eutrophic lakes (i.e., increasing organic carbon content) (Wahlgren, Chase and Alberts, 1979). The formation of Pu(IV)-organic ligand complexes appears to decrease the Pu(IV) adsorption onto suspended sediment; thus, the total dissolved Pu(IV) is increased, which in turn results in a decreased ratio of dissolved Pu(V,VI) to dissolved Pu(III,IV).

Wahlgren et al. (1977) concluded that while the concentration of the lower oxidation states is correlated with the dissolved organic carbon content of the waters, the concentration of plutonium in the higher oxidation states is correlated with the measured alkalinity. In the waters at this site, however, the percentage of plutonium in the higher oxidation states was not significantly correlated either negatively or positively with the measured alkalinity ($R^2 = 0.004$) or the dissolved organic carbon concentration ($R^2 = 0.36$). This suggests a more complex relationship in these waters, between the plutonium oxidation states and the characteristics of the water, perhaps due to the redox disequilibria and the redox reduction of the plutonium.

Although Pu(IV) may form stronger complexes with organic compounds in the waters than Pu(V) and Pu(VI), complexation with the organic compounds in the crib and spring may account for the mobile, anionic Pu(V,VI) charge form determined using the BLVWS. To evaluate the potential importance of organic complexation of Pu(V,VI) and to determine whether the anionic Pu(V,VI) charge form could be accounted for by organic complexation, the aqueous speciation of Pu(V,VI) was calculated using the thermodynamic data in Table 1 and assuming that the plutonium (V and/or VI) formed complexes with citrate and/or humic acid consistent with the estimated stability constants. The calculated speciation indicates that a majority of the aqueous plutonium in the higher oxidation states would exist as an organic complex, primarily as the PuO_2^+ -humate complex, which is expected to be anionically charged. Thus organic complexation of plutonium in the higher

oxidation states can account for the anionic charge form; however, the effects of organic complexation of Pu(IV) on the redox distribution and on these results need to be evaluated.

Particulate Concentration

A significant fraction (31 to 79 percent) of the total plutonium in the trench is attached to particulates (Table 4). The data suggest that the larger the fraction of the total plutonium attached to particulates, the larger will be the fraction of the dissolved plutonium in the lower oxidation states. In fact, the fraction of the total plutonium as particulates is significantly correlated with the percentage of dissolved plutonium in the higher or lower oxidation states ($R^2 = 0.95$), suggesting that the adsorption process is in equilibrium. Plutonium(IV) adsorbs much more strongly to particulates than Pu(VI) (Strickert, 1980). If the adsorption process is assumed to be in equilibrium, the ratio of plutonium particulate to dissolved Pu(IV) is 3.34 ± 2.19 . If the particulate concentration is known, then a K_d could also be calculated for comparison to reported values. A range of particulate concentrations of $1.0 \times 10^{-4} \text{ g ml}^{-1}$ to $1.0 \times 10^{-5} \text{ g ml}^{-1}$ would yield a K_d value of 10^4 to 10^5 ml g^{-1} consistent with those values reported in the literature for adsorption of Pu(IV) onto sediment at neutral pHs (Onishi et al., 1981).

Precipitation and Sorption

One important objective of studies at the low-level disposal site is identification of those mechanisms that retard the movement of plutonium in the groundwater. One potential mechanism is precipitation, either as a single component plutonium solid phase or as a coprecipitate with other solid phases. A second is sorption onto sediments. As the influent waters infiltrate through the trench bed and migrate in the groundwater to the seepage springs, plutonium appears to be efficiently removed from the water; the concentration of the plutonium in the spring is four to five orders of magnitude less than the concentration in the influent or trench waters. In fact, most of the attenuation occurs within the first few meters. This attenuation is most likely due to sorption of the Pu(IV),

which is produced as the plutonium migrates through the highly reducing environment of the trench bed (Robertson et al., 1983). This hypothesis is further supported by the small subsequent attenuation between the first well and the seepage springs. The geochemical model can be used to determine which solid phases are in equilibrium with or oversaturated with respect to these waters and thus potentially identify solid phases that could be sorption sinks for plutonium. By examining the changes in the calculated saturation indices between the influent and the spring it is also possible to determine which solid phases are dissolving or precipitating in these waters and thus might be important in removal of plutonium through coprecipitation. Comparison of the geochemical modeling results with the mineralogical analysis of the soils is discussed in Fruchter et al. (1984).

Formation of single component plutonium solid phases seems unlikely in these waters because all the plutonium solid phases are calculated to be undersaturated, if the plutonium is assumed to be distributed among the oxidation states in accordance with the analytical oxidation state measurements.

Coprecipitation of plutonium with other solid phases and sorption of plutonium onto solid phases could be important removal mechanisms. Past experimental work has shown that Pu(IV) sorbs onto rocks and minerals to a greater extent than Pu(V) and that Pu(IV) desorption is slow whereas Pu(V) desorption is rapid (Strickert, 1980). Complexation with humic acids may increase sorption because organic acids often occur as films on soil particles (Jenne, 1968). Bondiotti (1974) and Bondiotti, Reynolds and Shanks (1975) found that purified soil humates absorb plutonium strongly. Coprecipitates of transition metals have been noted with several commonly occurring solid phases, and sorption of metals by aluminosilicates is well recognized. However, further evaluation and collection of available experimental data is necessary before the importance of these factors for plutonium can be ascertained.

Solubility calculations for the groundwaters (i.e., the well and seepage spring waters) indicate that these waters are in equilibrium with

calcite (Appendix D). The presence of calcite in the soils is particularly important because several transition elements that form carbonate solid phases are known to coprecipitate with calcite when their concentrations are below the levels at which their distinct carbonate solid phases would form. Although no plutonium-containing carbonate solid phases have been identified, the potential for coprecipitation with calcite still exists. Laboratory studies indicate that Pu(III), Pu(IV) and Pu(V) precipitate with calcite (D. M. Nelson, personal communication, 1984). Gromov and Spitsyn (1974 a,b) reported that plutonium is strongly adsorbed to calcareous soils. This suggests that adsorption of plutonium on calcite could also be important, although the differences in adsorption may be due to a pH effect (Sanchez, 1983).

Aluminosilicates, particularly the zeolites, are very effective in removing ions including plutonium from solution through sorption (Rhodes 1952, 1957a,b; Evans, 1956; Tamura, 1972). Thus the presence of aluminosilicates and aluminum hydroxides in the groundwater system could account for the observed removal of plutonium. The saturation indices for both the influent and spring waters of 1981 and the single 1983 sample (i.e., last manway 2-15-83) for which both aluminum and silica values were available indicate that these waters are in equilibrium with allophane(a) (Appendix D). The groundwaters are calculated to be oversaturated with respect to halloysite, kaolinite, and gibbsite. The oversaturation, with respect to kaolinite and especially with respect to gibbsite, suggests that the analytically determined aluminum concentrations may be too high. The aluminum activity in soils is commonly controlled by at least one of these solid phases (Lindsay, 1979), and kaolinite has been identified in these soils. Overestimation of the aluminum concentration in solution by up to an order of magnitude or more is a common analytical problem unless a $<0.1 \mu\text{m}$ membrane filter is used, because of the presence of colloidal clay particles containing aluminum that pass through the $0.45 \mu\text{m}$ membranes (Kennedy, Zellweger and Jones, 1974). Another explanation for the calculated oversaturation is organic complexation of the aluminum. A conditional stability constant of approximately 14.0 to 16.0 between humate and aluminum would account for the observed oversaturation and result in

the solutions calculated to be in equilibrium. This stability constant is slightly larger than those for iron or copper, which appears to be in agreement with the data of Schnitzer and Skinner (1963), who found that more aluminum than iron was complexed by dissolved organic matter in soil solutions.

Ferrihydrite, $\text{Fe}(\text{OH})_3(\text{am})$, is an important scavenger of radionuclides, removing radionuclides from solution by sorption and coprecipitation. Using the analytically determined concentration for total dissolved iron and assuming iron redox equilibrium with the Eh measured using the platinum electrode, ferrihydrite was calculated to be oversaturated for several of the 1983 samples (Appendix D). Although ferrihydrite precipitates relatively rapidly from acid surface waters (Nordstrom, Jenne and Ball, 1979), it is frequently oversaturated in basaltic groundwaters (where the iron is suspected to result largely from the rusting of pipe). Thus it is unclear whether ferrihydrite oversaturation in these waters indicates excessively high analytical measurements. Kennedy, Zellweger and Jones (1974), however, observed that, as with aluminum, overestimation of the dissolved iron concentration can occur unless a 0.1- μm membrane is used to filter the water samples. Since iron has also been observed to be significantly complexed by soil organic matter (Schnitzer and Skinner, 1963), then oversaturation could be due to complexation by the dissolved organic compounds in the groundwater. Only one set of samples has detectable iron determinations for both the trench and the seepage springs (i.e., January 1983), and the calculated saturation indices suggest that ferrihydrite is precipitating. Given the sparseness of data, however, this cannot be stated with any certainty.

AMERICIUM

Analytical measurements of the americium concentration in the influent water and groundwater were made in 1983 (Table 4). Since the MINTEQ thermodynamic data base does not include data for americium, no comparison was made between the calculated speciation and analytical measurements. Americium is associated with particulates in the influent water to a greater extent than plutonium, although when the particulate plutonium is

compared to the dissolved Pu(III,IV) concentration, the fractions are similar. In the groundwater, the fraction of the total americium associated with particulates is also higher than for plutonium. The dominant aqueous species of americium in the pH range from 4 to 8, according to Onishi et al. (1981), would be the cationic species, AmSO_4^+ , and AmOH_2^+ . At neutral pH, Kd values for adsorption of americium are quite large. Nevissi and Schell (1975) observed that at Bikini Atoll, 93 percent of the americium was associated with particulates and was transported in ocean waters with these particles. As with plutonium, the total concentration of americium in the waters decreases by as much as five orders of magnitude en route from the trench to the seepage springs. This large attenuation is most likely due to adsorption onto the sediments since americium is strongly sorbed to particulates.

CONCLUSIONS AND RECOMMENDATIONS

The data collected at this site with regard to plutonium have provided some valuable insights into the behavior of plutonium in groundwater. First, the concentration of plutonium is reduced by nearly four to five orders of magnitude between the influent or trench and the seepage springs. Most of this decrease occurs within the first few meters, apparently due to rapid reduction of the Pu(V,VI) to Pu(III,IV) in the highly reducing sediments of the trench and the rapid removal mostly of Pu(IV) by sorption onto the sediments. Second, plutonium is not in redox equilibria in the groundwater and actually appears to be undergoing redox during migration from the trench to the seepage springs. This redox is in agreement with the geochemical modeling results, which suggest that the lower oxidation states would be dominant in this system. Third, the migrating plutonium species is anionic, probably due to the formation of an anionic organic complex. Fourth, the influent waters appear to be in a state of redox quasi-equilibrium, as indicated by the very strong correlation between the percentage of the total plutonium that is associated with particulates and the percentage of dissolved plutonium that is in the higher or lower oxidation states. On the basis of comparison of the analytical data from the site with the results of the geochemical modeling, it appears that neither the thermodynamic data presented in Table 1 nor that in the compilation of Lemire and Tremaine (1980) can adequately describe the aqueous speciation of plutonium in these waters. The discrepancy between the analytical measurements and the thermodynamic calculations may be due to the dynamics of the redox equilibria (i.e., the reduction) and/or to inadequate or missing thermodynamic data for the carbonate and organic complexes of plutonium.

Americium is also efficiently removed in the groundwater and has decrease in concentration of nearly four to five orders of magnitude between the influent or trench and the seepage springs. Most of the removal occurs in the first few meters of the groundwater and is most likely due to adsorption since americium is strongly adsorbed on sediments. The mobility of americium in the groundwater appears to be controlled closely by adsorption.

Although the studies reported above have provided valuable insights into the behavior of plutonium in this groundwater system, there are still several areas of research pertaining to plutonium that need to be addressed in order to eventually permit prediction of the behavior of plutonium in other groundwater systems. First, evaluation must be made of the kinetics of plutonium redox reactions in natural systems and also of the importance of such factors as particulates, type of particulates and/or the influence of the solution chemistry on the kinetics. Second, additional research is needed to provide a more accurate and consistent thermodynamic data base for plutonium. Specifically, this research should seek to elucidate the importance of carbonate and organic ligand complexes and to estimate the appropriate thermodynamic data to describe these complexes. As additional solubility data become available, validation studies such as those for uranium (Krupka, Jenne and Deutsch, 1983) and copper (Cowan, in preparation) will need to be completed. Finally, the relative importance of coprecipitation and adsorption in natural systems, especially as those processes affect the mobility and retention of plutonium in the groundwater, needs to be evaluated. Included in this research would be identification of the most important solid phases and/or adsorption sinks for plutonium.

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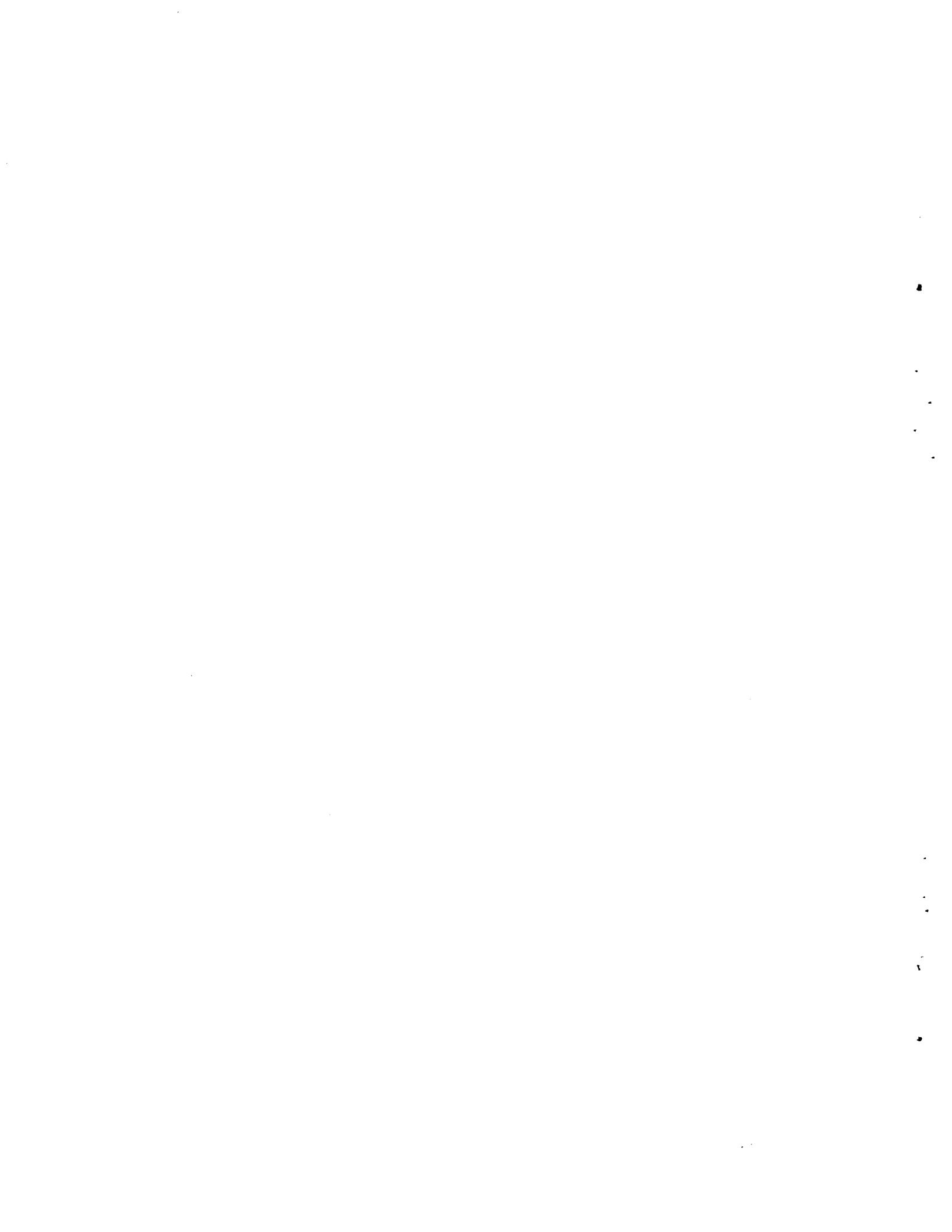
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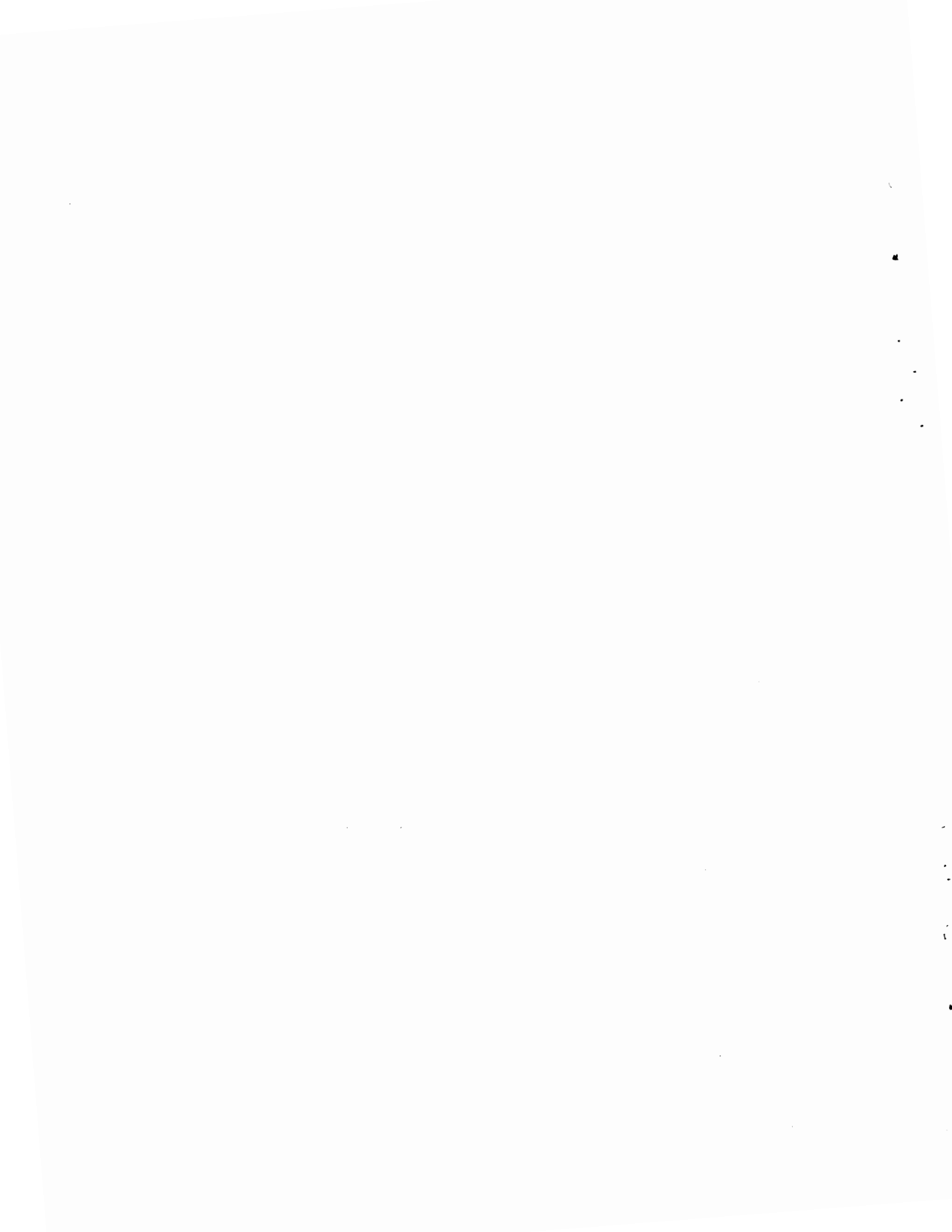
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APPENDIX A

THERMODYNAMIC DATA FOR PLUTONIUM AQUEOUS SPECIATION



APPENDIX A

THERMODYNAMIC DATA FOR PLUTONIUM AQUEOUS SPECIATION

The thermodynamic data presented in Table 1 is based in part on the preliminary plutonium data base for MINTEQA compiled by Schwab and Felmy (unpublished). Their thermodynamic data base has been modified to correct for recording and computational errors and in one case to incorporate a more reliable reference. Furthermore, their compilation did not include correction to zero ionic strength because of a lack of agreement on the method for calculating the corrections, in particular those from very high ionic strengths. The accepted values presented here were corrected to zero ionic strength using the Davies equation, although it is recognized that these corrections may not be valid for ionic strengths above 0.1 M and definitely are not valid above 1 M. Since this is the method used in MINTEQA to calculate the effect of ionic strength, this correction at least ensures that the log K values will be correct at the ionic strength at which they were measured. This appendix is used to document the sources of the thermodynamic data reported in Table 1 and any assumptions and corrections to the original experimental data. It is not intended to be a critical review of the plutonium thermodynamic data.

REDOX COUPLES

The equilibrium constants for the redox couples of plutonium are calculated from the $\Delta H_{f,298}^0$, $\Delta G_{f,298}^0$ and S_{298}^0 values for α -Pu, Pu^{3+} , Pu^{4+} , PuO_2^+ and PuO_2^{2+} presented in Table A.1. These values are taken from Fuger and Oetting (1976), and the reader is referred to that paper for a detailed critique of the values.

HYDROLYSIS SPECIES

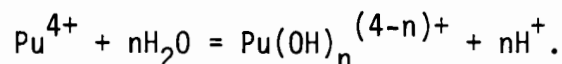
No hydrolysis species of Pu^{3+} are included in the thermodynamic data base because the log K value for PuOH^{2+} , the only hydrolysis species postulated, was not determined directly but estimated from stability constants for similar species.

TABLE A-1. Thermodynamic Values for the Plutonium Ionic Species and α -Pu (Fuger and Oetting, 1976)

Species	$\Delta H_{f,298}^{\circ}$ (kcal mol ⁻¹)	$\Delta G_{f,298}^{\circ}$ (kcal mol ⁻¹)	ΔS_{298}° (cal mol ⁻¹ k ⁻¹)
α -Pu	0.0(a)	0.0(a)	13.42 ± 0.10
Pu ³⁺	-141.5 ± 0.5	-138.3 ± 0.8	-44.1 ± 2.0
Pu ⁴⁺	-128.2 ± 0.8	-115.1 ± 0.8	-93.0 ± 5
PuO ₂ ⁺	-218.6 ± 1.7	-203.1 ± 1.8	-5 ± 2
PuO ₂ ²⁺	-196.5 ± 1.6	-180.9 ± 1.9	-21 ± 2

(a) By definition

The hydrolysis constants for Pu⁴⁺ were calculated from the stepwise hydrolysis constants determined by Metivier (1973) at unit ionic strength. The stepwise constants log B_i are -0.45, -0.75, -3.3 and -6.3, respectively. The cumulative constants, log K_n, are -0.45, -1.2, -4.5, -10.8, respectively, for the equilibria



Correcting these values back to zero ionic strength, using the Davies equation, yields 0.11, -0.18, -3.28, and -9.48 respectively for the log K_n values. Baes and Mesmer (1976) extrapolate a log K value for Pu(OH)₅⁻ from the log K values for the other hydrolysis species. Since there is no evidence that this species is formed in solution, it was not included in the data base.

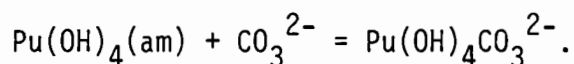
Thermodynamic data to represent the formation of the PuO₂OH⁰ species was not included in the data base because of questions concerning the validity of the experimental method used to determine the log K value and the inability to confirm the measurement by extrapolation from, or comparison with, constants for similar species.

The hydrolysis values for PuO₂²⁺ were taken from the study of Schedin (1975). He found that the (PuO₂)₂(OH)₂²⁺ and (PuO₂)₄(OH)₇ species formed with log K_{2,2} = -8.23 and log K_{4,7} = -29.11 at I=0.

CARBONATES

Although there is some qualitative data available on the formation of Pu(III)-carbonates, estimates of the formation constants are unavailable.

Schwab and Felmy reinterpreted the data of Moskvina and Gel'man (1958) on $\text{Pu(OH)}_4(\text{am})$ solubility as a function of CO_3 concentration and determined that the complex formed was more likely $\text{Pu(OH)}_4\text{CO}_3^{2-}$ than PuCO_3^{2+} . They calculated a log K of -3.36 at I=10 for the equilibria



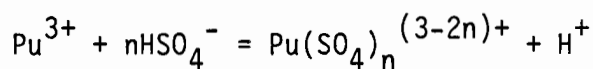
Calculation of the log K in terms of H_2O and Pu^{4+} using the solubility of $\text{Pu(OH)}_4(\text{am})$ and correcting to zero ionic strength using the Davies equation yields -3.48.

No information was found on the formation of Pu(V)-carbonates.

Although there is evidence that Pu(IV)-carbonate species do form, the reported constants vary widely and are internally inconsistent; therefore, no values were included in the thermodynamic data base.

SULFATES

Two Pu(III)-sulfate species have been identified. The thermodynamic data to represent the formation of PuSO_4^+ and $\text{Pu(SO}_4)_2^-$ is from Vasudeva Rao et al. (1978). They calculated log K values of 0.676 and 0.812 for the formation of $\text{Pu(SO}_4)_2^-$ and PuSO_4^+ , respectively, according to the equilibria



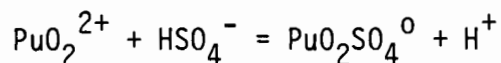
at I=1.0. Correction to zero ionic strength and recalculation of the log K in terms of SO_4^{2-} yields log K = 5.47 and 3.614, respectively, for $\text{Pu(SO}_4)_2^-$ and PuSO_4^+ .

The thermodynamic data to represent the formation of Pu(IV)-sulfate complexes is taken from Bagawde, Ramakrishna and Patil (1976). They give log K values of 2.832 and 4.651 for the formation of PuSO_4^0 and $\text{Pu(SO}_4)_2^0$, respectively, from Pu^{4+} and HSO_4^- in 2 M NaClO_4 . Correction to zero ionic

strength using the Davies equation, and recalculation of the log K value in terms of SO_4^{2-} yields 4.819 and 8.709, respectively.

No information was found on the formation of Pu(V)-sulfate species.

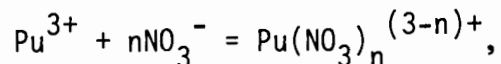
The only Pu(VI)-sulfate species included in the data base is $\text{PuO}_2\text{SO}_4^0$. The thermodynamic data to represent this species was taken from Patil and Ramakrishna (1976), who determined that the log K value for the equilibria



was 1.158 in 2 M HClO_4 . Correction to zero ionic strength and recalculation of the log K value as above in terms of SO_4^{2-} yields a log K of 1.387.

NITRATES

The thermodynamic data for the three Pu(III)-nitrate species is taken from Shevchenko, Timoshev and Volkova (1959). For the equilibria



they determined log K_n values of 0.77, 1.16, and 1.16, respectively, in a 1 M solution of HNO_3 and HClO_4 . With correction to zero ionic strength, using the Davies equation, the log K values are calculated to be 1.41, 2.22, and 2.52 for the formation of PuNO_3^{2+} , $\text{Pu}(\text{NO}_3)_2^+$ and $\text{Pu}(\text{NO}_3)^0$, respectively.

The log K for the formation of Pu(IV)-nitrate species were determined by Bagawde, Ramakrishna and Patil (1976). The log K values are 0.647 and 1.117 for the formation of PuNO_3^{3+} and $\text{Pu}(\text{NO}_3)_2^{2+}$, respectively at $I=2$. Correction to zero ionic strength yields 0.54 and 1.00 respectively.

No thermodynamic data were located for Pu(V)-nitrate species.

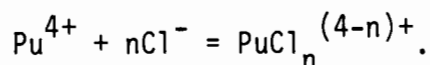
Mazumdar and Sivaramakrishnan (1965) determined a log K value of -0.027 to represent the formation of $\text{PuO}_2\text{NO}_3^+$ from PuO_2^{2+} and NO_3^- at $I=4.1$. Correction to zero ionic strength yields a log K of -1.14.

CHLORIDES

The log K value to represent the formation of PuCl^{2+} from Pu^{3+} and Cl^- was determined by Ward and Welch (1956) to be -1.187 at zero ionic

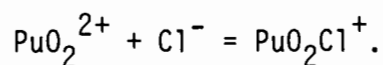
strength. The log K value for the formation of PuCl_2^+ was estimated by Ward and Welch (1956), but the data did not allow an accurate calculation of this constant; therefore, it was not included in the data base.

Bagawde, Ramakrishna and Patil (1976) determined log K values of 0.152 and -0.64 in 2 M NaClO_4 to represent the formation of PuCl^{3+} and PuCl_2^{2+} , respectively, according to the equilibria



Correction of the log K values to zero ionic strength yields log K = 0.094 and -0.74, respectively.

The log K value to represent the PuO_2Cl^+ complex was determined by Newton and Baker (1957) in 2 M HCl and NaClO_4 to be 0.097 for the equilibria

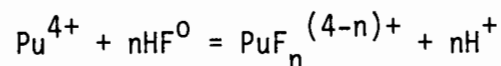


Correction of the log K to $I=0$, using the Davies equation, yields 0.068. This data source is different from that chosen by Scwab and Felmy, who used the data of Mazumdar and Sivaramakrishnan (1965). The log K value for the second chloride complex of PuO_2^{2+} is taken from Mazumdar and Sivaramakrishnan (1965). They determined a log K value of -0.77 at $I=4.1$ for the formation of this species from PuO_2^{2+} and Cl^- . Correction to zero ionic strength yields -2.07.

FLUORIDES

There are no reliable quantitative data available for Pu(III)-F complexes.

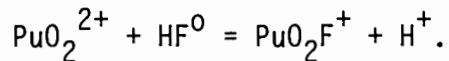
The formation of Pu(IV)-fluoride complexes was studied by Bagawde, Ramakrishna and Patil (1976). They reported log K values for the equilibria



in 2 M NaClO_4 of 4.640 and 7.6212 for PuF^{3+} and PuF_2^{2+} , respectively.

Correcting to zero ionic strength and rewriting the equilibria in terms of F^- resulted in a log K values of 7.566 and 13.687, respectively, for n=1 and 2.

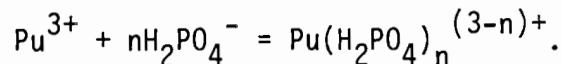
The thermodynamic data to represent the formation of the PuO_2F^+ complex were taken from Patil and Ramakrishna (1976). They determined that the log K value for the formation of this species was 1.079 in 2 M $NaClO_4$ according to the equilibria



Correcting to zero ionic strength, using the Davies equation, and rewriting the equilibria in terms of F^- yields a log K of 4.0337.

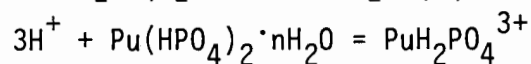
PHOSPHATES

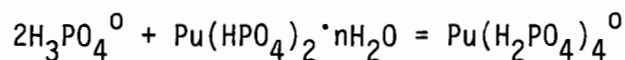
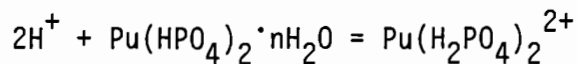
Moskvin (1971) determined log K values for the four phosphate species of Pu^{3+} at I=1.0. However, only the values for the first two species were accepted because the log K values for the third and fourth species were estimated from very little data. The log K values for the first two species are 1.48, and 2.20 for the formation of $PuHPO_4^{2+}$, and $Pu(HPO_4)_2^+$, respectively, according to the equilibria



Correcting to zero ionic strength and rewriting the equilibria in terms of PO_4^{3-} yields 21.643 and 42.306, respectively.

The log K values adopted to represent the formation of the Pu^{4+} -phosphate species are based on a recalculation, by Schwab and Felmy (unpublished), of the data by King (1949) and Denotkina and Shevchenko (1967). The original researchers assumed that the Pu^{4+} -phosphate species involved complexation with HPO_4^{2-} ; however, they could not determine a unique set of constants to represent the data. Schwab and Felmy assumed that the complexing ligand was $H_2PO_4^-$ and were able to determine a unique set of constants that represented the data very well. They determined log K values of -6.37, -4.85 and -3.32, respectively, for the formation of $PuH_2PO_4^{3+}$, $Pu(H_2PO_4)_2^{2+}$ and $Pu(H_2PO_4)_4^0$ according to the equilibria





at I=2.08. Correcting to I=0 and rewriting the equilibria in terms of PO_4^{3-} and Pu^{4+} yield 24.49, 47.43 and 92.12, respectively.

Although Denotkina and Shevchenko (1967) determined a log K value for the formation of the Pu(VI)-phosphate species, $\text{PuO}_2(\text{H}_2\text{PO}_4)^+$, lack of critical support for their critical assumptions led Schwab and Felmy to reject their value. Thus, no thermodynamic data are included in the data base for Pu(IV)-phosphate species.

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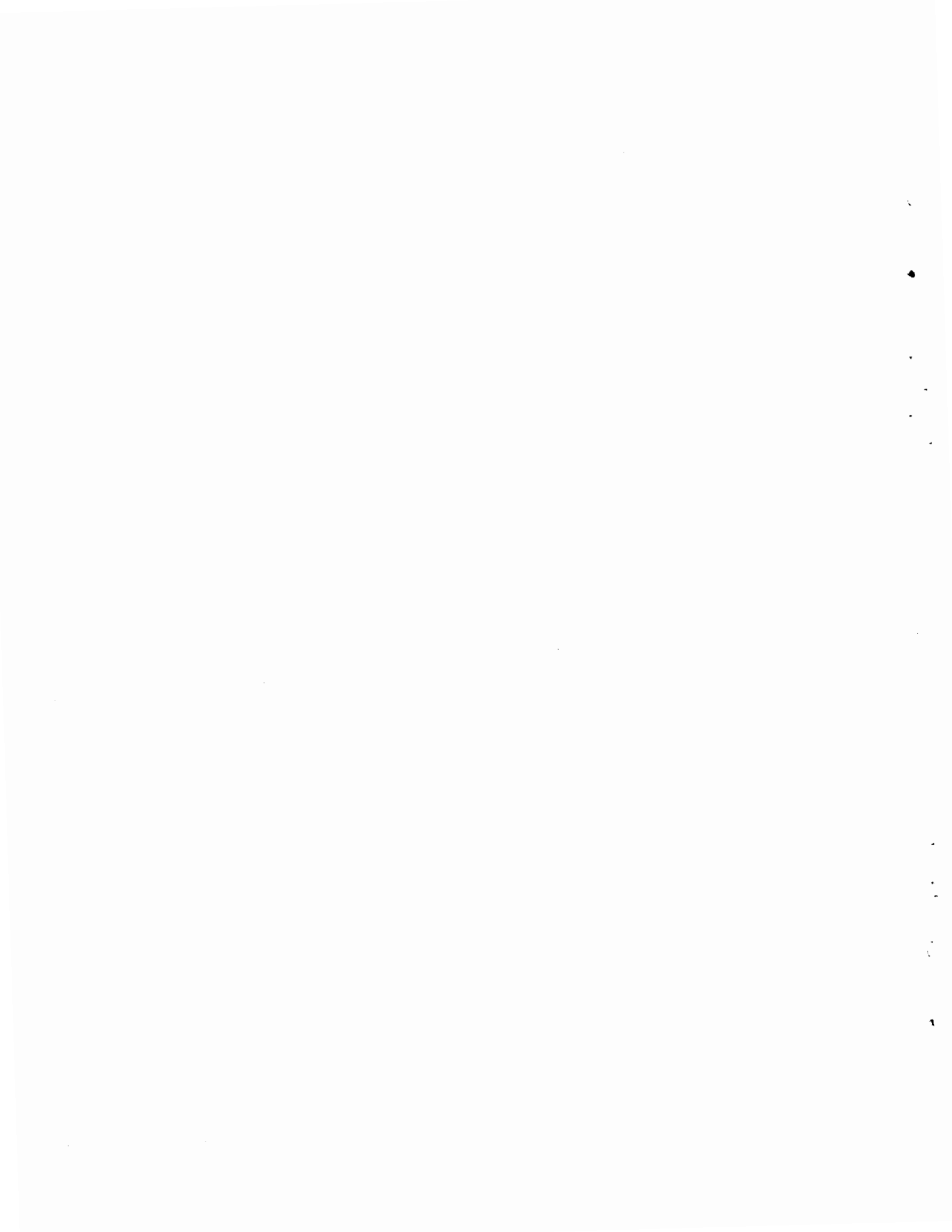
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APPENDIX B

CHEMICAL COMPOSITION OF TRENCH, WELL
AND SPRING WATERS FOR 1983^(a)

^(a) Fruchter, J., et al., 1984. Radionuclide Migration in Groundwater: Annual Report for FY 1983. NUREG/CR-3712, Prepared for the U.S. Nuclear Regulatory Commission by Pacific Northwest Laboratory, Richland, Washington.



CHEMICAL COMPOSITION OF TRENCH, WELL AND SPRING WATERS,
JANUARY, 1983

CONSTITUENT	TRENCH 1/26/83	WELL #1 1/27/83	WELL #3 1/28/83	SPRING 1/28/83	SPRING 1/31/83
TEMPERATURE °C	21	18	18	20	20
pH	7.30	8.10	8.15	8.10	8.15
Eh (mv)	+406	+430	+356	+436	+385
DISSOLVED O ₂ (mg/l)	8.9	7.2	9.2	4.9	4.5
ALKALINITY (As CaCO ₃ -mg/l)	38.0	54.9	52.8	57.5	57.7
DOC (mg/l)	<1	<1	<1	<1	<1
Ca (mg/l)	16.3	25.2	25.3	26.0	20.1
Mg (mg/l)	4.0	4.2	4.2	4.3	4.8
Na (mg/l)	1.68	1.70	1.70	1.99	2.17
K (mg/l)	0.40	1.0	1.0	0.50	1.8
Sr (mg/l)	0.081	0.093	0.093	0.094	0.12
SO ₄ ⁻² (mg/l)	14.3	13.9	12.2	13.5	13.9
S ⁻ (POLAROGRAPHIC) (mg/l)	<0.003	<0.003	<0.003	<0.003	<0.003
SO ₄ ⁻² (TOTAL BY ICP) (mg/l)	5.6	5.1	5.1	5.4	4.6
NO ₃ ⁻ (mg/l)	9.2	13.2	8.2	12.5	13.2
NO ₂ ⁻ (mg/l)	2.5	<0.05	<0.05	<0.05	<0.05
F ⁻ (mg/l)	<0.15	<0.15	<0.15	<0.15	<0.15
PO ₄ ⁻³ (mg/l)	3.8	<0.2	<0.2	<0.2	<0.2
P (TOTAL BY ICP) (mg/l)	1.48	<0.1	<0.1	<0.1	<0.1
Cl ⁻ (mg/l)	0.90	0.87	0.70	0.83	0.87
Si (mg/l)	1.8	4.4	4.4	2.9	8.2
Al (µg/l)	<50	<50	<50	<50	<50
As (µg/l)	<30	<30	<30	<30	<30
B (µg/l)	10	10	10	10	10
Ba (µg/l)	34	28	26	16	14
Co (µg/l)	<10	<10	<10	<10	<10
Cr (µg/l)	<10	<10	<10	<10	<10
Fe (TOTAL BY ICP) (µg/l)	110	<20	<20	<20	<20
Fe ⁺² (COLORIMETRIC) (µg/l)	8.1	<2*	6.1*	3.6	<2
Fe ⁺³ (COLORIMETRIC) (µg/l)	84.9	<2*	5.9*	2.5	<2
Fe ⁺² /Fe ⁺³	0.067	-	1.03	1.44	-
Li (µg/l)	<5	<5	<5	<5	<5
Mn (µg/l)	<10	<10	<10	<10	<10
Mo (µg/l)	<10	<10	<10	<10	<10
Ni (µg/l)	<20	<20	<20	<20	<20
Se (µg/l)	<100	<100	<100	<100	<100
Tl (µg/l)	<10	<10	<10	<10	<10
V (µg/l)	<5	<5	<5	<5	<5
Zn (µg/l)	24	<10	<10	<10	<10

*WATER PUMPED THROUGH STAINLESS STEEL SAMPLING DEVICE - PROBABLE CONTAMINATION WITH IRON

CHEMICAL COMPOSITION OF TRENCH, WELL AND SPRING WATERS,
FEBRUARY, 1983

CONSTITUENT	TRENCH (1st MANWAY) 2/15/83	TRENCH (LAST MANWAY) 2/15/83	WELL #1 2/15/83	WELL #3 2/17/83	SPRINGS 2/17/83
TEMPERATURE °C	17	15	15	19	21
pH	9.20	9.25	8.15	8.40	8.10
Eh (mv)	+155	+150		+350	+340
DISSOLVED O ₂ (mg/l)	6.58	5.91	5.57	6.64	5.14
ALKALINITY (As CaCO ₃ -mg/l)	63.3	63.0	65.5	53.7	57.1
DOC (mg/l)	0.4	0.7	0.4	2.3	0.3
Ca (mg/l)	15.5	16	23	21	26
Mg (mg/l)	3.9	4.0	4.0	4.9	4.4
Na (mg/l)	1.63	1.72	2.11	2.23	1.82
K (mg/l)	0.4	0.4	0.4	1.2	0.8
Sr (mg/l)	0.082	0.083	0.089	0.12	0.097
SO ₄ ⁻² (mg/l)	10.0	6.7	14.6	8.8	12.5
S ⁻ (POLAROGRAPHIC) (mg/l)	<1 x 10 ⁻⁵	<1 x 10 ⁻⁵	<1 x 10 ⁻⁵	<1 x 10 ⁻⁵	2 x 10 ⁻⁵
SO ₄ ⁻² (TOTAL BY ICP) (mg/l)	6.2	6.4	7.6	4.7	6.0
NO ₃ ⁻ (mg/l)	1.3	1.3	16.3	8.0	13.5
NO ₂ ⁻ (mg/l)	3.4	1.7	<0.03	<0.03	<0.03
F ⁻ (mg/l)	<0.08	<0.08	<0.08	<0.08	<0.08
PO ₄ ⁻³ (mg/l)	<0.2	<0.2	<0.2	<0.2	<0.2
P (TOTAL BY ICP) (mg/l)	<0.1	<0.1	<0.1	<0.1	0.18
Cl ⁻ (mg/l)	0.59	0.40	0.97	0.55	0.88
Si (mg/l)	1.74	1.80	2.88	8.50	4.50
Al (µg/l)	<30	100	<30	70	100
As (µg/l)	<20	<20	<20	<20	<20
B (µg/l)	20	20	10	20	20
Ba (µg/l)	30	31	14	16	30
Cr (µg/l)	<10	<10	<10	<10	<10
Fe (TOTAL BY ICP) (µg/l)	30	30	<5	20	10
Fe ⁺² (COLORIMETRIC) (µg/l)	<2	<2	2	<2	<2
Fe ⁺³ (COLORIMETRIC) (µg/l)	19	18	2	15	3
Li (µg/l)	<5	<5	<5	<5	<5
Mn (µg/l)	<3	<3	3	<3	<3
Mo (µg/l)	<10	<10	<10	<10	<10
Ni (µg/l)	<20	20	<20	20	20
Se (µg/l)	<100	<100	<100	<100	<100
Tl (µg/l)	<5	<5	<5	<5	<5
V (µg/l)	<5	<5	<5	8	<3
Zn (µg/l)	37	11	<5	<5	<5

CHEMICAL COMPOSITION OF TRENCH, WELL AND SPRING WATERS,
MARCH, 1983

CONSTITUENT	TRENCH (1st MANWAY) 3/30/83	TRENCH (LAST MANWAY) 3/30/83	WELL #1 3/31/83	SPRINGS 4/1/83
TEMPERATURE °C	22.0	23.0	20.0	21.5
pH	8.58	8.70	8.25	8.10
Eh (mv)	+245	+265	+355	+365
DISSOLVED O ₂ (mg/l)	5.59	4.71	6.09	4.78
ALKALINITY (As CaCO ₃ -mg/l)	41.8	41.0	53.7	55.8
Ca (mg/l)	13.9	12.9	26.3	25.7
Mg (mg/l)	3.2	3.3	4.0	4.0
Na (mg/l)	1.7	1.5	2.1	1.9
K (mg/l)	0.8	0.7	1.0	1.4
Sr (mg/l)	0.072	0.087	0.095	0.095
SO ₄ ⁻² (mg/l)	12.7	11.3	12.1	11.8
S ⁻ (POLAROGRAPHIC) (mg/l)	0.205	0.163	0.215	0.163
SO ₄ ⁻² (TOTAL BY ICP) (mg/l)	12.9	11.7	12.9	12.6
NO ₃ ⁻ (mg/l)	2.1	3.0	16.8	13.6
NO ₂ ⁻ (mg/l)	1.9	2.6	<0.05	<0.05
F ⁻ (mg/l)	<0.1	<0.01	<0.1	<0.1
PO ₄ ⁻³ (mg/l)	<0.2	<0.2	<0.02	<0.2
P (TOTAL BY ICP) (mg/l)	<0.1	<0.1	<0.1	<0.1
Cl ⁻ (mg/l)	1.0	0.95	1.1	0.89
Si (mg/l)	2.3	2.1	3.5	5.5
Al (µg/l)	<30	<30	<30	<30
As (µg/l)	30	<20	<20	<20
B (µg/l)	22	25	<10	<10
Ba (µg/l)	36	35	16	31
Fe (TOTAL BY ICP) (µg/l)	20	61	<10	<10
Fe ⁺² (COLORIMETRIC) (µg/l)	<2	6	<2	<2
Fe ⁺³ (COLORIMETRIC) (µg/l)	18	59	2	4
Li (µg/l)	<10	<10	<10	<10
Mn (µg/l)	<3	<3	<3	<3
Mo (µg/l)	<10	<10	<10	<10
Ni (µg/l)	<20	<20	<20	<20
Se (µg/l)	<100	<100	<100	<100
Ti (µg/l)	<5	<5	<5	<5
V (µg/l)	<5	<5	<5	<5
Zn (µg/l)	10	10	<10	20

CHEMICAL COMPOSITION OF TRENCH, WELL AND SPRING WATERS,
MAY, 1983

CONSTITUENT	TRENCH (2nd MANWAY) 5/5/83	TRENCH (LAST MANWAY) 5/5/83	WELL #1 5/6/83	SPRINGS 5/9/83
TEMPERATURE °C	21.0	19.0	28.5	22.0
pH	9.10	8.70	8.05	7.90
Eh (mv)	+155	-315	+335	-355
DISSOLVED O ₂ (mg/l)	4.84	4.56	1.95	3.91
ALKALINITY (As CaCO ₃ -mg/l)	46.0	48.4	64.1	59.9
Ca (mg/l)	13.8	16.9	31.1	25.7
Mg (mg/l)	3.2	3.8	4.7	4.0
Na (mg/l)	1.8	2.2	2.8	1.9
K (mg/l)	0.9	1.1	1.5	1.4
Sr (mg/l)	0.078	0.096	0.12	0.095
SO ₄ ⁻² (mg/l)	14.3	12.6	20.0	11.8
S ⁻ (POLAROGRAPHIC) (mg/l)	0.163	0.197	0.160	0.139
SO ₄ ⁻² (TOTAL BY ICP) (mg/l)	13.5	17.7	18.6	12.6
NO ₃ ⁻ (mg/l)	3.2	4.1	22	14.3
NO ₂ ⁻ (mg/l)	9.3	6.6	<0.05	0.05
F ⁻ (mg/l)	<0.1	<0.1	<0.1	<0.1
PO ₄ ⁻³ (mg/l)	<0.2	<0.2	<0.2	<0.2
P (TOTAL BY ICP) (mg/l)	0.1	<0.1	0.1	<0.1
Cl ⁻ (mg/l)	0.77	1.0	1.0	0.89
Si (mg/l)	2.1	2.5	4.9	5.5
Al (µg/l)	<30	<30	30	30
As (µg/l)	<20	<20	<20	20
B (µg/l)	<10	25	<10	10
Ba (µg/l)	28	19	23	31
Cr (µg/l)	<20	<20	<20	20
Fe (TOTAL BY ICP) (µg/l)	41	16	71*	10
Fe ⁺² (COLORIMETRIC) (µg/l)	<2	2	4*	3
Fe ⁺³ (COLORIMETRIC) (µg/l)	32	12	67*	24
Li (µg/l)	<10	<10	<10	<10
Mn (µg/l)	<3	<3	<3	<3
Mo (µg/l)	<10	<10	<10	<10
Ni (µg/l)	<20	<20	<20	20
Se (µg/l)	<100	<100	<100	100
Ti (µg/l)	<5	<5	<5	<5
V (µg/l)	<5	<5	<5	<5
Zn (µg/l)	<5	<5	67	20

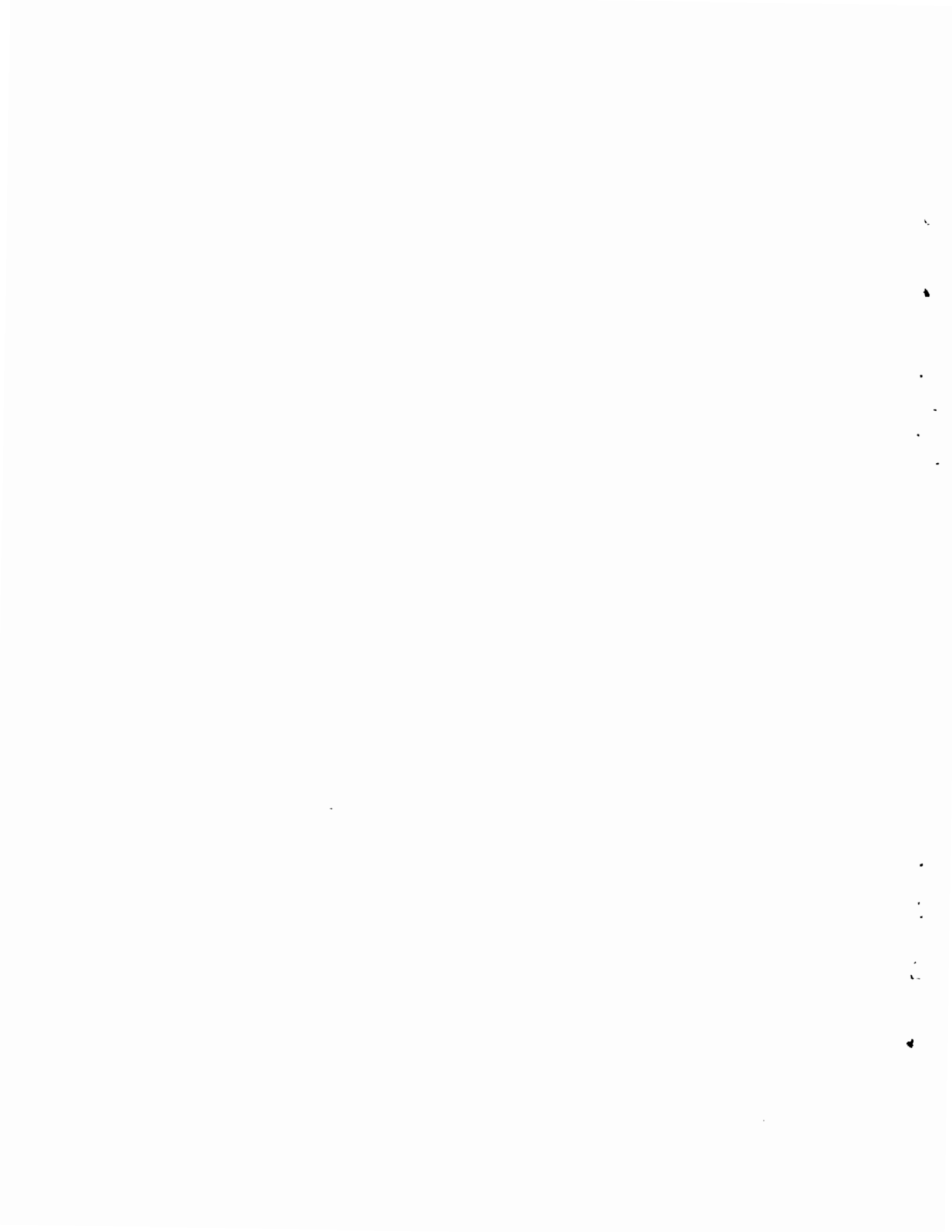
*SAMPLED WITH IEA PUMP HAVING STAINLESS STEEL COMPONENTS - POSSIBLE CONTAMINATION

CHEMICAL COMPOSITION OF TRENCH AND SPRING WATERS,
JUNE, 1983

CONSTITUENT	TRENCH	TRENCH	SPRINGS
	(2nd MANWAY) 6/16/83	(LAST MANWAY) 6/16/83	6/20/83
TEMPERATURE °C	19.5	20.5	24.8
pH	7.30	7.20	7.90
Eh (mv)	+195	+180	+275
DISSOLVED O ₂ (mg/l)	6.68	7.06	4.55
ALKALINITY (As CaCO ₃ -mg/l)	36.5	39.7	58.2
Ca (mg/l)	14.7	14.8	27.3
Mg (mg/l)	3.3	3.4	4.2
Na (mg/l)	1.9	1.9	2.2
K (mg/l)	0.8	0.8	1.4
Sr (mg/l)	0.079	0.079	0.10
SO ₄ ⁻² (mg/l)	15.2	15.0	14.5
S ⁻ (POLAROGRAPHIC) (mg/l)	0.061	0.078	0.068
SO ₄ ⁻² (TOTAL BY ICPI) (mg/l)	15.3	15.3	15.3
NO ₃ ⁻ (mg/l)	0.73	1.2	15.5
NO ₂ ⁻ (mg/l)	0.60	0.80	-0.05
F ⁻ (mg/l)	<0.1	<0.1	-0.1
PO ₄ ⁻³ (mg/l)	0.80	1.1	-0.2
P (TOTAL BY ICPI) (mg/l)	0.6	0.7	-0.1
Cl ⁻ (mg/l)	1.0	1.6	1.0
Si (mg/l)	2.4	2.4	5.7
Al (µg/l)	<30	<30	<30
As (µg/l)	<20	<20	<20
B (µg/l)	<10	<10	<10
Be (µg/l)	29	29	32
Cr (µg/l)	<20	<20	<20
Fe (TOTAL BY ICPI) (µg/l)	16	20	<10
Fe ⁻² (COLORIMETRIC) (µg/l)	5.9	7.6	<1
Fe ⁻³ (COLORIMETRIC) (µg/l)	7.6	9.5	3.5
Li (µg/l)	<10	<10	<10
Mn (µg/l)	<3	<3	<3
Mo (µg/l)	<10	<10	<10
Ni (µg/l)	<20	<20	<20
Se (µg/l)	<100	<100	<100
Tl (µg/l)	<5	<5	<5
V (µg/l)	<5	<5	<5
Zn (µg/l)	10	10	<10

CHEMICAL COMPOSITION OF TRENCH, WELL AND SPRING WATERS,
SEPTEMBER, 1983

CONSTITUENT	TRENCH	WELL #1	SPRINGS
	(2nd MANWAY) 9/9/83	9/9/83	9/12/83
TEMPERATURE °C	23.0	32.0	32.0
pH	7.80	8.20	8.0
Eh (mv)	+190	+300	+385
DISSOLVED O ₂ (mg/l)	6.00	2.08	4.17
ALKALINITY (As CaCO ₃ -mg/l)	44.0	63.3	58.2
DOC (mg/l)	0.70	0.62	0.44
Ca (mg/l)	16.8	27.5	24.3
Mg (mg/l)	3.9	4.1	3.7
Na (mg/l)	2.1	3.8	3.3
K (mg/l)	0.64	1.7	1.6
Sr (mg/l)	0.093	0.104	0.093
SO ₄ ⁻² (mg/l)	17	18	13
S ⁻ (POLAROGRAPHIC) (mg/l)	0.039	0.458	1.15
SO ₄ ⁻² (TOTAL BY ICPI) (mg/l)	18.9	18.6	14.1
NO ₃ ⁻ (mg/l)	2.9	13.1	11.0
NO ₂ ⁻ (mg/l)	1.1	0.05	-0.05
F ⁻ (mg/l)	-0.25	-0.25	-0.25
PO ₄ ⁻³ (mg/l)	-	-	-
P (TOTAL BY ICPI) (mg/l)	<0.1	0.17	0.1
Cl ⁻ (mg/l)	0.97	0.97	0.86
Si (mg/l)	1.8	5.3	6.9
Al (µg/l)	<30	<30	<30
As (µg/l)	<20	<20	<20
B (µg/l)	20	20	20
Be (µg/l)	29	15	27
Cr (µg/l)	<20	20	<20
Fe (TOTAL BY ICPI) (µg/l)	35	<10	<10
Fe ⁻² (COLORIMETRIC) (µg/l)	15.3	4.2	2.9
Fe ⁻³ (COLORIMETRIC) (µg/l)	20.6	<2	4.9
Li (µg/l)	<10	10	10
Mn (µg/l)	<3	3	3
Mo (µg/l)	<10	<10	<10
Ni (µg/l)	<20	<20	<20
Se (µg/l)	<100	<100	<100
Tl (µg/l)	<5	<5	<5
V (µg/l)	<5	<5	<5
Zn (µg/l)	<10	<10	16



APPENDIX C

LOW-MOLECULAR-WEIGHT ORGANIC COMPOUNDS AND
TOTAL DISSOLVED ORGANIC CARBON CONCENTRATIONS
IN TRENCH, WELL AND SPRING WATERS FOR 1983^(a)

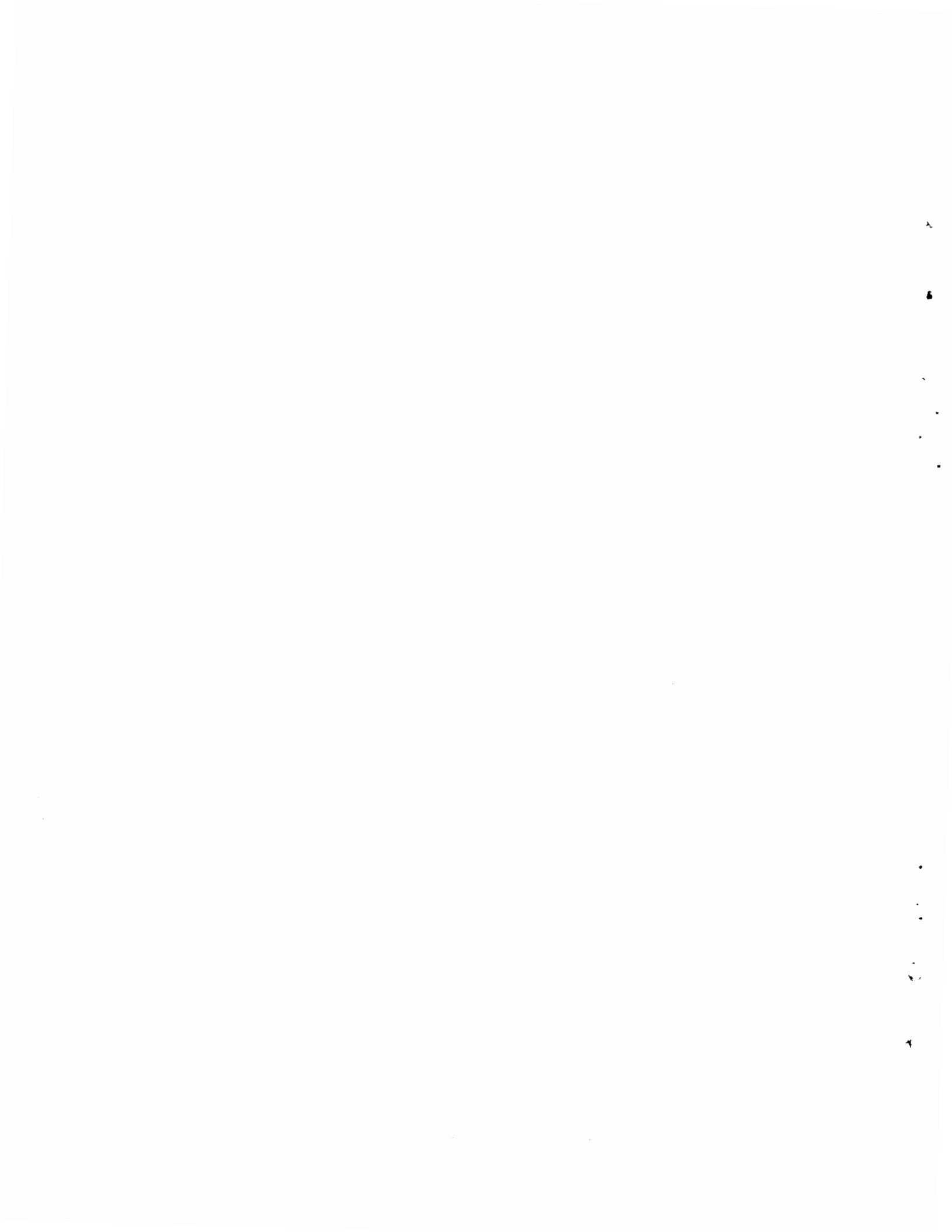
^(a) Fruchter, J., et al., 1984. Radionuclide Migration in Groundwater: Annual Report for FY 1983. NUREG/CR-3712, Prepared for the U.S. Nuclear Regulatory Commission by Pacific Northwest Laboratory, Richland, Washington.



TABLE C-1. Low-Molecular-Weight Organics and Total Dissolved Organic Carbon (ppb)

<u>Location</u>	<u>Date</u>	<u>Dicarboxylic Acids</u>	<u>Monocarboxylic Acids</u>	<u>Oxygenated Acids</u>	<u>Aromatic Acids</u>	<u>TOC</u>
Manway #1	2/15/83	20.6	37.7	2.7	3.2	2,500
	3/30/83	3.6	18.5	1.4	1.0	16,700
Manway #2	5/5/83	6.8	11.4	2.8	3.5	16,100
	6/16/83	5.9	12.3	1.2	2.7	15,200
Manway #10	2/15/83	3.4	6.7	0.5	0.8	1,700
	6/16/83	6.3	11.0	2.7	2.1	1,800
Well #1	2/15/83	0.9	5.6	0	0	13,000
	5/6/83	3.7	7.9	0	1.4	19,100
Well #3	2/17/83	2.7	11.6	0	0.3	9,900
Springs	2/17/83	1.4	12	0	0	8,000
	5/9/83	2.1	4.8	0.3	0.6	4,200
	6/20/83	3.0	4.4	1.2	1.0	17,000

C.1



APPENDIX D

CALCULATED SATURATION INDICES FOR SELECTED SOLIDS^(a)

^(a) Fruchter, J., et al., 1984. Radionuclide Migration in Groundwater: Annual Report for FY 1983. NUREG/CR-3712, Prepared for the U.S. Nuclear Regulatory Commission by Pacific Northwest Laboratory, Richland, Washington.

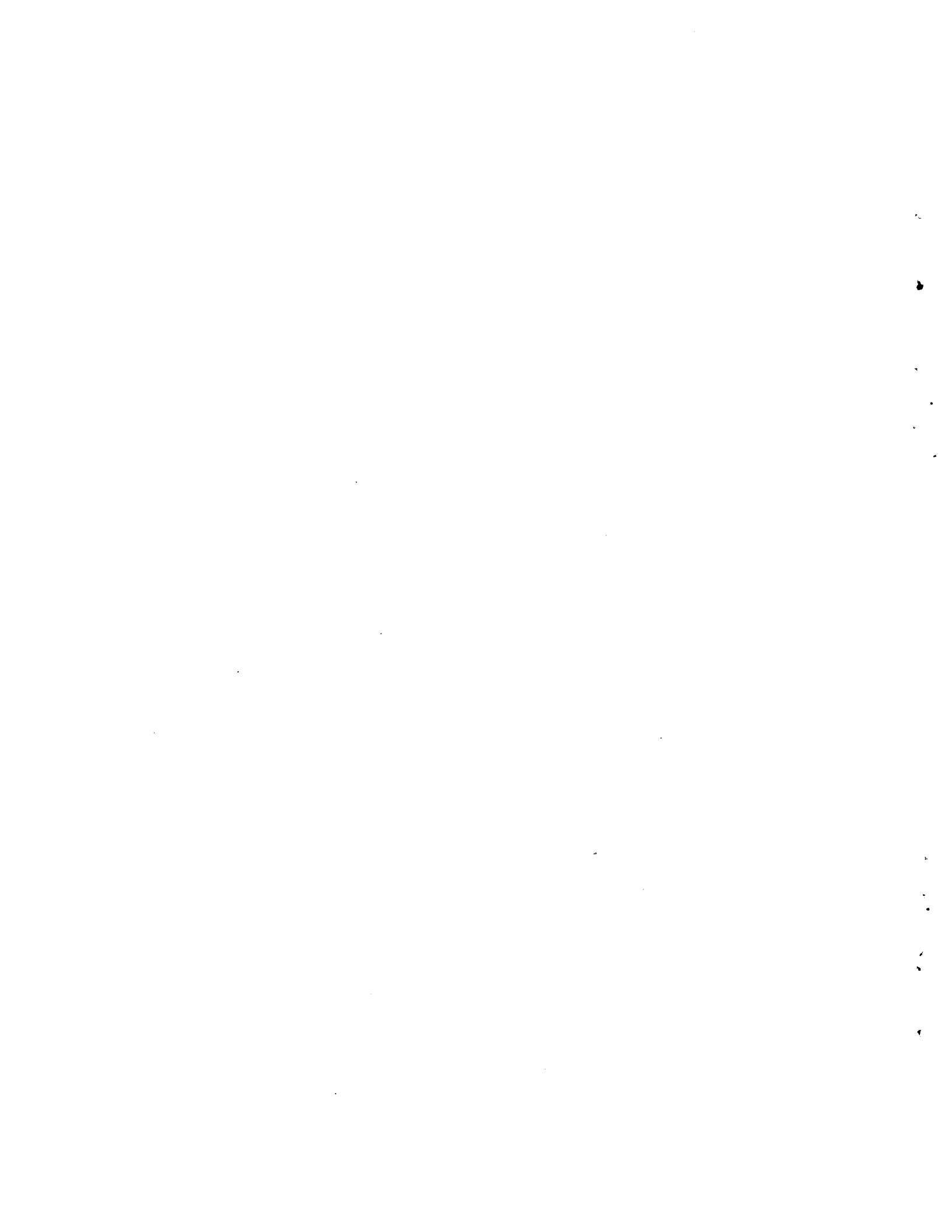


TABLE D-1. Calculated Saturation Indices

<u>Sample Date</u>	<u>Sample Location</u>	<u>Calcite</u>	<u>Quartz</u>	<u>Christobalite</u>
3/81	Influent	-1.039	<u>0.043</u>	-0.400
	Spring	<u>-0.301</u>	0.312	<u>-0.126</u>
6/81	Influent	-1.682	<u>0.019</u>	-0.413
	Spring	<u>-0.068</u>	-0.329	<u>-0.099</u>
1/83	Manway 1	-1.046	-0.126	-0.552
	Well 1	<u>0.043</u>	0.306	<u>-0.126</u>
	Well 3	<u>0.079</u>	0.305	<u>-0.126</u>
	Spring (1)	<u>0.104</u>	<u>0.093</u>	-0.335
	Spring (2)	<u>0.046</u>	0.543	<u>-0.115</u>
2/83	Manway 1	0.882	<u>-0.129</u>	-0.563
	Manway 10	0.911	<u>-0.082</u>	-0.519
	Well 1	<u>0.083</u>	<u>0.171</u>	-0.267
	Well 3	<u>0.265</u>	0.571	<u>0.141</u>
	Spring	<u>0.115</u>	0.267	<u>-0.159</u>
3/83	Manway 1	<u>0.203</u>	<u>-0.051</u>	-0.476
	Manway 10	<u>0.291</u>	<u>-0.113</u>	-0.536
	Well 1	<u>0.226</u>	<u>0.172</u>	-0.256
	Spring	<u>0.110</u>	0.346	<u>-0.079</u>
5/83	Manway 2	0.676	<u>-0.110</u>	-0.537
	Manway 10	<u>0.411</u>	<u>0.030</u>	-0.400
	Well 1	<u>0.288</u>	<u>0.188</u>	-0.225
	Spring	<u>-0.047</u>	0.341	-0.084
6/83	Manway 2	-1.117	<u>0.023</u>	-0.406
	Manway 10	-1.164	<u>0.007</u>	-0.420
	Spring	<u>0.003</u>	0.312	<u>-0.107</u>
9/83	Manway 2	-0.438	-0.159	-0.582
	Well 1	<u>0.426</u>	0.165	-0.241
	Spring	<u>0.156</u>	0.284	-0.123

*½ detection limit

TABLE D-2. Calculated Saturation Indices

<u>Sample Date</u>	<u>Sample Location</u>	<u>Anorthite</u>	<u>Albite</u>
3/81	Influent	-4.352	-1.821
	Spring	-2.309	-0.310
6/81	Influent	-4.820	-2.351
	Spring	-1.996	-0.396
1/83	Manway 1	-3.994	-2.495
	Well 1	-2.496	-0.928
	Well 3	-2.462	-0.913
	Spring (1)	-2.821	-1.483
	Spring (2)	-2.007	<u>-0.081</u>
2/83	Manway 1	-3.747	-2.306
	Manway 10	-1.981	-1.284
	Well 1	-3.441	-1.513
	Well 3	<u>-0.975</u>	0.506
	Spring	<u>-1.237</u>	-0.394
3/83	Manway 1	-3.668	-2.156
	Manway 10	-3.819	-2.406
	Well 1	-3.044	-1.415
	Spring	-2.718	-0.962
5/83	Manway 2	-3.774	-2.276
	Manway 10	-3.423	-1.757
	Well 1	-2.944	-1.355
	Spring	-2.787	-1.016
6/83	Manway 2	-4.368	-2.291
	Manway 10	-4.401	-2.354
	Spring	-2.766	-1.048
9/83	Manway 2	-3.968	-2.486
	Well 1	-3.063	-1.344
	Spring	-2.871	-1.049

TABLE D-3. Calculated Saturation Indices

<u>Sample Date</u>	<u>Sample Location</u>	<u>Allophane (A)</u>	<u>Allophane (F)</u>	<u>Kaolinite</u>
3/81	Influent	<u>0.023*</u>	0.915*	5.167*
	Spring	<u>0.133*</u>	1.105*	5.356*
6/81	Influent	<u>0.204*</u>	0.568*	5.704*
	Spring	-0.336*	0.660*	5.849*
1/83	Manway 1	<u>-0.392</u>	0.476	4.955
	Well 1	<u>-0.395</u>	0.601	4.946
	Well 3	-0.419	-0.585	4.876
	Spring (1)	-0.564	0.432	4.429
	Spring (2)	-0.529	0.475	5.252
2/83	Manway 1	-1.338	<u>-0.166</u>	1.825
	Manway 10	<u>-0.333*</u>	0.847*	3.660*
	Well 1	-0.451	0.553	4.219
	Well 3	<u>-0.218</u>	0.826	5.853
	Spring	<u>-0.100</u>	0.896	5.923
3/83	Manway 1	-1.290	<u>-0.218</u>	2.703
	Manway 10	-1.498	<u>-0.406</u>	2.257
	Well 1	-0.838	<u>0.182</u>	3.900
	Spring	-0.830	<u>0.166</u>	4.401
5/83	Manway 2	-1.675	-0.519	1.672
	Manway 10	-1.100	<u>-0.008</u>	2.901
	Well 1	-1.392	-0.404	3.599
	Spring	-0.737	<u>0.227</u>	4.686
6/83	Manway 2	-0.478	0.390	4.754
	Manway 10	-0.500	0.352	4.830
	Spring	-0.949	0.015	4.441
9/83	Manway 2	-0.837	0.111	3.793
	Well 1	-1.834	-0.822	2.940
	Spring	-1.623	-0.643	3.576

All used $\frac{1}{2}$ detection limit except *.

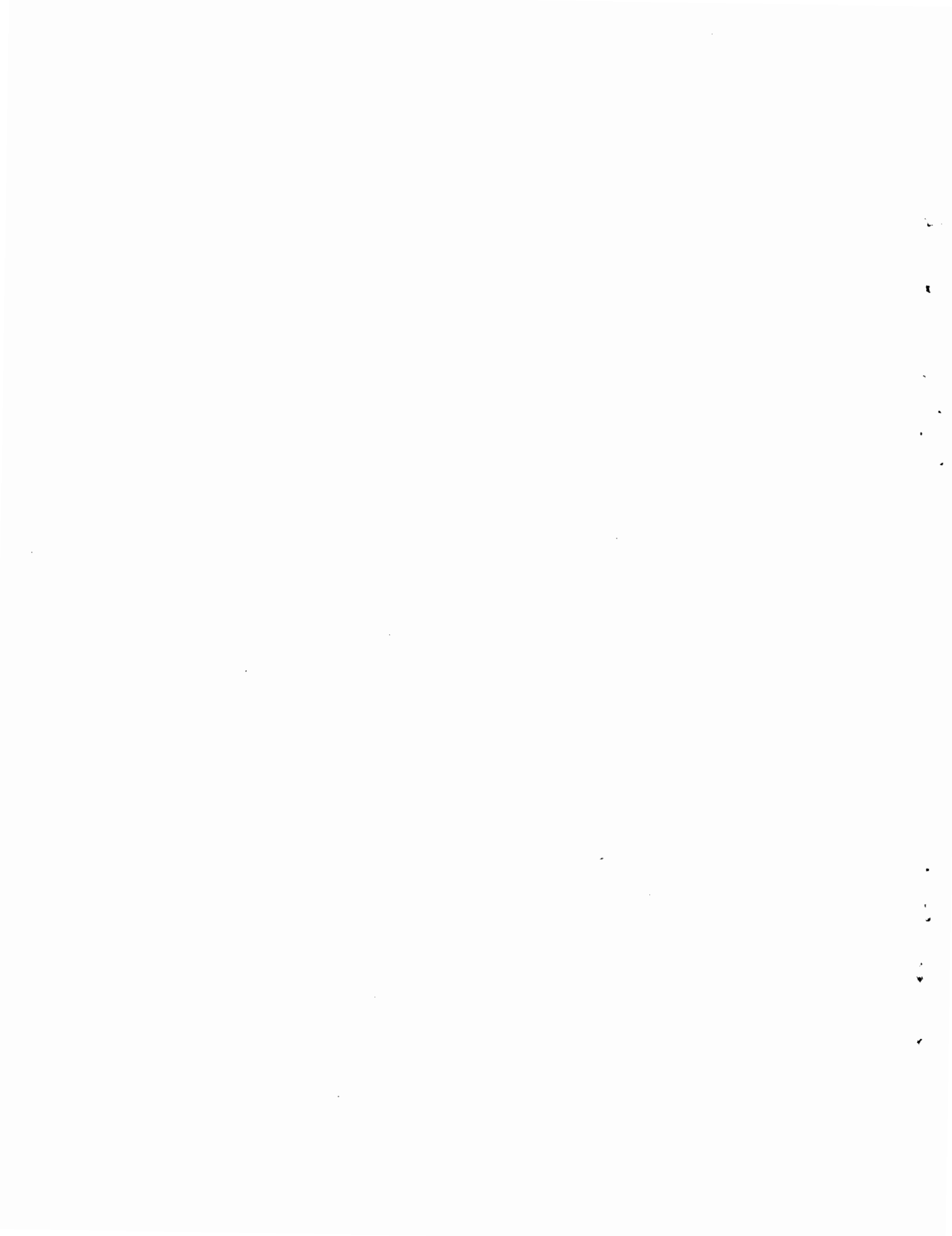
TABLE D-4. Calculated Saturation Indices

<u>Sample Date</u>	<u>Sample Location</u>	<u>Gibbsite</u>	<u>Mont-CA</u>	<u>Halloysite</u>
3/81	Influent	0.675	<u>0.187</u>	1.750
	Spring	0.740	1.635	2.462
6/81	Influent	0.950	0.755	2.357
	Spring	0.461	1.351	2.032
1/83	Manway 1	0.713	<u>0.027</u>	1.643
	Well 1	<u>0.285</u>	0.781	1.600
	Well 3	<u>0.250</u>	0.715	1.529
	Spring (1)	<u>0.234</u>	<u>-0.028</u>	1.105
	Spring (2)	0.195	1.533	1.928
2/83	Manway 1	-0.838	-3.145	-1.533
	Manway 10	<u>0.037*</u>	-1.003*	<u>0.279*</u>
	Well 1	<u>0.065</u>	<u>-0.357</u>	0.838
	Well 3	0.470	2.319	2.518
	Spring	0.804	1.985	2.610
3/83	Manway 1	-0.490	-2.036	-0.598
	Manway 10	-0.654	-2.566	-1.033
	Well 1	<u>-0.110</u>	-0.486	0.576
	Spring	<u>-0.038</u>	<u>0.336</u>	1.094
5/83	Manway 2	-0.944	-3.182	-1.640
	Manway 10	0.464	-1.758	<u>-0.434</u>
	Well 1	<u>-0.298</u>	-0.554	<u>0.369</u>
	Spring	<u>0.110</u>	0.613	1.385
6/83	Manway 2	0.468	<u>-0.073</u>	1.425
	Manway 10	0.519	<u>-0.001</u>	1.512
	Spring	<u>0.008</u>	<u>0.348</u>	1.171
9/83	Manway 2	<u>0.160</u>	-1.124	0.503
	Well 1	-0.614	-1.183	<u>-0.253</u>
	Spring	-0.415	<u>-0.359</u>	<u>0.382</u>

TABLE D-5. Calculated Saturation Indices

<u>Sample Date</u>	<u>Sample Location</u>	<u>Ferrihydrite Fe(OH)₃</u>	<u>Fe₃(OH)₈</u>	<u>Greenalite</u>
3/81	Influent	1.726*	2.554*	-0.522*
	Spring	1.189*	-1.532*	-8.941*
6/81	Influent	-3.218*	-9.835*	-7.879*
	Spring	-0.220*	-6.313*	-14.616*
1/83	Manway 1	2.247	<u>0.094</u>	-11.079
	Well 1	1.478*	-3.447*	-16.317*
	Well 3	1.466	-2.232	-12.604
	Spring (1)	1.478	-3.529	-16.925
	Spring (2)	1.466*	-2.753*	-13.628
2/83	Manway 1	1.190	<u>-0.635</u>	-7.057
	Manway 10	1.143	<u>-0.703</u>	-6.950
	Well 1	0.864*	-3.761*	-13.943*
	Well 3	1.660	-1.817	-11.957
	Spring	1.478	-1.904	-11.670
3/83	Manway 1	1.545	-0.567	-8.670
	Manway 10	1.939	<u>0.139</u>	-9.006
	Well 1	1.131	-3.349	-14.147
	Spring	1.177	-3.239	-13.696
5/83	Manway 2	1.419	<u>0.091</u>	-6.091
	Manway 10	1.356	-2.428	-13.051
	Well 1	2.336	0.766	-8.739
	Spring	1.187	-2.840	-12.559
6/83	Manway 2	0.729	-1.122	-5.368
	Manway 10	0.090	-2.426	-5.443
	Spring	1.183	-1.513	-8.520
9/83	Manway 2	1.851	2.056	-2.821
	Well 1	1.148	-2.390	-11.022
	Spring	1.190	-3.467	-14.261

*_{1/2} detection limit



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