



U.S. Department of Energy

Richland Operations Office
P.O. Box 550
Richland, Washington 99352

0047414

046010

MAY 9 1997

Mr. Steve M. Alexander
Perimeter Areas Section Manager
Nuclear Waste Program
State of Washington
Department of Ecology
1315 W. Fourth Avenue
Kennewick, Washington 99336-6018



Dear Mr. Alexander:

EQUIVALENCY DEMONSTRATION FOR 100-D PONDS

The attached document supports the 100-D Ponds Closure Plan, currently being revised. This equivalence demonstration will be included in the revised 100-D Ponds Closure Plan, scheduled to be transmitted to the State of Washington Department of Ecology (Ecology) in July 1997, and included in the 1998 modification to the Hanford Facility Resource Conservation and Recovery Act Permit for Treatment, Storage, and Disposal of Dangerous Wastes. Transmittal of this equivalency demonstration now will allow Ecology time to review the technical arguments supporting the clean closure of this unit.

The equivalency demonstration was written to address the following issues:

- The possibility that discharges to 100-D Ponds contaminated the groundwater beneath the ponds; and
- The possibility that contaminants from 100-D Ponds activities migrated through the vadose zone and were deposited at depth.

The issue of soil contamination at depth is unresolved at this time. Personnel from the Kennewick Ecology office have expressed concern that waste disposal activities at 100-D Ponds may have deposited contamination at depth, and have requested that soil samples from boreholes be retrieved from the surface to the groundwater table and analyzed. This concern was prompted by a Westinghouse Hanford Company report released in 1993 that tendered a conceptual model invoking a "geochemical trap" in which heavy metals precipitated beneath the ponds. This conceptual model was not supported or tested with site-specific chemical data or modeling results. The attached report provides data from chemical analyses from 1996 remedial actions at 100-D Ponds and geochemical modeling to refute the presence of heavy metal precipitates in the vadose zone beneath the ponds.

PNL, 1994, *Hanford Site Environmental Data for Calendar Year 1993 – Surface and Columbia River*, PNL-9824, Pacific Northwest Laboratory, Richland, Washington.

Peterson, R.E., R.F. Raidle, and C.W. Denslow, 1996, *Conceptual Site Models for Groundwater Contamination at 100-BC-5, 100-KR-4, 100-HR-3, and 100-FR-3 Operable Units*, BHI-00917, Bechtel Hanford, Inc., Richland, Washington.

Price, S.M., 1989, "Metallic Mercury Discovered at 189-D," Westinghouse Hanford Company, Richland, Washington.

Wilson, D.W., 1990, "Designation of 284-E Powerhouse Flyash," WHC Internal Memo No. 92941-90-033, dated May 2, 1990, Westinghouse Hanford Company, Richland, Washington.

Mr. Steve M. Alexander

-2-

046010
MAY 9 1997

If you have any questions, please contact me on 376-9552.

Sincerely,



Glenn I. Goldberg, Project Manager
Remedial Actions Project

RAP:GIG

Attachment

cc w/encl:

C. E. Corriveau, BHI
C. W. Hedel, CHI
K. K. Holliday, Ecology
J. R. James, BHI
S. W. Petersen, CHI

8.0 REFERENCES

- Alexander, D.J., 1993, *Groundwater Impact Assessment Report for the 100-D Ponds*, WHC-EP-0666, Westinghouse Hanford Company, Richland, Washington.
- BHI, 1995, *Data Evaluation: 100-D Ponds*, BHI-00328, Rev. 1, Bechtel Hanford, Inc., Richland, Washington.
- DOE-RL, 1992, *Long-Term Storage and Disposal of Coal-Fired Steam Plant Ash on the Hanford Site*, DOE/RL-RPB-192, U.S. Department of Energy, Richland Operations Office, Richland, Washington.
- DOE-RL, 1995, *2101-M Pond Closure Plan*, DOE/RL-88-41, Rev. 2a, U.S. Department of Energy, Richland Operations Office, Richland, Washington.
- DOE-RL, 1996a, *Hanford Site Background: Part 3, Groundwater Background*, DOE/RL-96-61, Draft A, U.S. Department of Energy, Richland Operations Office, Richland, Washington.
- DOE-RL, 1996b, *Sampling and Analysis Plan for the 100-D Ponds Voluntary Remediation Project*, DOE/RL-96-43, Rev. 1, U.S. Department of Energy, Richland Operations Office, Richland, Washington.
- Ecology, EPA, and DOE, 1996, *Hanford Federal Facility Agreement and Consent Order*, 2 vols., as amended, Washington State Department of Ecology, U.S. Environmental Protection Agency, and U.S. Department of Energy, Olympia, Washington.
- Falcone, and H.H. Schobert, 1986, "Mineral transformations during ashing of selected low-rank coals," in *Mineral Matter and Ash in Coal*, Karl S. Vorres, ed., American Chemical Society, Washington, D.C., pp. 115-127.
- Gano, K.A. and M.J. Lauterbach, 1990, *Estimate of Mercury Released to 120-D-1 (100-D) Pond*, Westinghouse Hanford Company, Richland, Washington.
- Hartman, M.J., 1996, *100-D Ponds Groundwater Quality Assessment*, WHC-SD-EN-EV-033, Westinghouse Hanford Company, Richland, Washington.
- Huffman, G.P. and F.E. Huggins, 1986, "Reactions and transformations of coal mineral matter at elevated temperatures," in *Mineral Matter and Ash in Coal*, Karl S. Vorres, ed., American Chemical Society, Washington, D.C., pp. 101-113.
- Parkhurst, D.L., 1995, *User's Guide to PHREEQC - A Computer Program for Speciation, Reaction-Path, Advective-Transport, and Inverse Geochemical Calculations*, Water-Resources Investigations Report 95-4227, U.S. Geological Survey, Lakewood, Colorado.

0052097

~~11-5-95~~ 4/10/97

EQUIVALENCY DEMONSTRATION FOR 100-D PONDS

Scott Petersen, CHI
April, 1997

Ponds, allowing more time for infiltrating water to be in contact with the ash and more completely approach equilibrium.

Data collected from different depths show that soil contamination in 100-D Ponds was restricted to the upper layer of sediment (Figure 4), as COCs are not elevated in the ash immediately underlying the sediment. A geochemical model was employed to evaluate the possibility that contaminants were transported through the upper portions of the vadose zone and deposited in sedimentary deposits beneath 100-D Ponds. This process was postulated by Alexander (1993) in a hydrochemical conceptual model that suggested that the abrupt changes in mineralogy between the coal ash-Ringold interface would create a "geochemical trap" for cationic heavy metals. This argument was purely qualitative and based on some questionable assumptions. For instance, coal ash was invoked as the source for the heavy metals, but analyses of the ash have shown very low values for leachable heavy metals (DOE-RL, 1992; Wilson, 1990). Leachate compositions of samples from surface sediment in the settling pond also show very low levels of leachable heavy metals (e.g., <0.1 ppm lead, <0.02 ppm chromium; BHL, 1995).

The geochemical model PHREEQC was employed to simulate subsurface reactions between water infiltrating from 100-D Ponds and minerals in the vadose zone and saturated zone. The input parameters were chosen to represent an upper bound of values for heavy metals (using results of TCLP analyses from contaminated surface sediments) and caustic conditions (using portlandite as the calcium oxide phase) in the ash beneath the ponds. Results from this quantitative geochemical analysis show only a trace amount of precipitation of heavy metal-containing minerals at the water table. Most COC-containing minerals are strongly undersaturated, and would not be expected to precipitate.

Results from the PHREEQC model do not perfectly match conditions measured beneath the ponds. For example, the modeled solution has a final pH of 9.7 after mixing with groundwater and precipitation of minerals in the saturated zone. Recent measurements from monitoring wells downgradient of 100-D Ponds had average pH values of 9.3, although some measurements were as high as 9.9 (Hartman, 1996). Calcium is markedly higher in the modeled solution than in prevailing groundwater conditions, and iron is lower. With the exception of these deviations, results from the modeled solution correspond closely to those in the groundwater and do not indicate that large amounts of minerals containing heavy metals are present in the subsurface beneath the ponds.

The chemical and modeling data support the argument that most or all of the COCs discharged to 100-D Ponds were immobilized in the flocculent and sediment deposited on the surface of the settling pond. This sediment was removed in August, 1996, and samples collected from the bottom of the ponds after this removal show no evidence of contamination in the coal ash. The cleanup action, empirical data, and modeling results indicate that the contamination at 100-D Ponds has been successfully remediated and requires no further action.

CONTENTS

1.0	INTRODUCTION	1
2.0	REGULATORY BACKGROUND	1
3.0	DESCRIPTION OF UNIT AND WASTE CHARACTERISTICS	1
3.1	CONTAMINANTS DEPOSITED IN 100-D PONDS	4
4.0	PHYSICAL AND CHEMICAL FACTORS AFFECTING CONTAMINANT MIGRATION	5
4.1	FLOCCULENTS IN WATER TREATMENT	5
5.0	EVALUATION OF GROUNDWATER DATA	6
5.1	GROUNDWATER QUALITY	6
6.0	EVALUATION OF SUBSURFACE SOILS	8
6.1	DATA FROM NEAR-SURFACE SAMPLES	8
6.2	MODELING OF SUBSURFACE SOIL	11
6.2.1	The Computer Program PHREEQC	11
6.2.2	Application of PHREEQC to 100-D Ponds	11
7.0	CONCLUSIONS	14
8.0	REFERENCES	17

FIGURES

1.	Location of 100-D Ponds and Monitoring Wells	2
2.	Cross Section Through 100-D Ponds	3
3.	Conductivity and Chromium Values from 100-D Ponds Monitoring Wells from December, 1991 to December, 1996	9
4.	Concentration Profile of Several Constituents in 100-D Ponds Sediment and Underlying Ash	10

TABLES

1.	Statistical Summary of Groundwater Samples from Monitoring Wells Downgradient of 100-D Ponds	7
2.	Summary Statistics and Compliance with Cleanup Limits for August, 1996, Verification Data	12
3.	Results from Geochemical Modeling of 100-D Ponds, Using PHREEQC	15

Table 3. Results from Geochemical Modeling of 100-D Ponds, Using PHREEQC. Solution compositions in mg/L.

Analyte	Beginning Solution, Col. R. water + TCLP*	Solution after Reaction w/ ash	Solution after Reaction w/ Ringold	Ave. Upgradient, Well D5-13	Mix 10% Ringold 90 % Upgradient	Solution, Mixed water w/ Ringold	Average Comp. of Downgradient Wells
Al	1.28E-03	3.28E-26	9.90E-02	8.10E-02	8.28E-02	2.51E-01	2.60E-01
As	1.00E-01	8.92E-02	8.92E-02	4.30E-03	1.28E-02	1.29E-08	2.61E-03
Ba	3.00E-02	6.46E-07	6.46E-07	8.00E-02	7.20E-02	3.69E-02	2.96E-02
Ca	21.25	5599.2	5567.1	43.73	596.0	218.04	25.46
Cd	5.00E-03	5.00E-03	5.00E-03	6.70E-03	6.53E-03	6.53E-03	0.00E+00
Cl	1	1.000399	1.000399	11.801305	10.72	10.720080	3.31
Cr	1.50E-02	1.50E-02	1.50E-02	7.50E-02	6.91E-02	6.90E-02	6.43E-02
F	1.00E-01	1.00E-01	1.00E-01	2.93E-01	2.74E-01	2.74E-01	1.92E-01
Fe	3.50E-02	7.84E-07	1.19E-03	2.52E-01	2.27E-01	1.49E-09	6.01E-01
Hg	2.00E-04	2.00E-04	2.00E-04	2.00E-04	2.00E-04	2.00E-04	8.60E-05
K	1.1	1.10	1.10	3.56	3.32	3.31	3.00
Mg	5.1	7.20E-06	1.14E-03	111.024	99.94	5.64E-09	3.50
N	2.00E-01	2.00E-01	2.00E-01	23.41	21.10	21.09	2.03
Na	2.15	2.15	38.37	5.66	8.932	8.856	4.29
Pb	1.00E-01	1.00E-01	1.00E-01	5.00E-03	1.45E-02	7.83E-04	2.61E-03
S	11	281.2	281.2	17.59	43.94	43.935900	22.86
Sb	3.20E-02	3.20E-02	3.20E-02	0.00E+00	3.20E-03	3.20E-03	6.01E-02
Si	17.8	3455.1	3457.9	5.21	350.3	2.876416	
V	2.00E-03	2.00E-03	2.00E-03	0.00E+00	2.00E-04	2.00E-03	1.07E-02
Zn	1.00E-03	1.00E-03	1.00E-03	1.56E-02	1.42E-02	1.41E-02	7.80E-03
pH=	8.6	12.328	12.328	7.98	11.861	9.659	8.46
		mg/kg				mg/kg	
Precipitate:	Ca-nontronite	0.061			Ba3(AsO4)2	0.059	
	Ba3(AsO4)2	0.05			Anorthite	2316	
	Hematite	0.027			Albite	0.53	
	Sepiolite	32.2			Calcite	110.2	
	Anorthite		218.6		Montmorillonite	3147	
	Quartz		187.0		Pb(OH)2	0.016	
Reactant:	Anhydrite	624.5	Albite	413.1	Hematite	148.6	
	Portlandite	9670	Calcite	0.448	Quartz	2198	
	Quartz	7398	Mont.	0.0358	Boehmite	1869	

* Average TCLP analyses of sediments for Ba, Cd, Cr, Hg, Pb, Sb, V, and Zn.

1.0 INTRODUCTION

The purpose of this equivalency demonstration is to evaluate the possibility that discharges into the 100-D Ponds treatment, storage, and/or disposal (TSD) unit affected the subsurface soils and groundwater in the area. This will be accomplished by evaluating the groundwater data collected to date during monitoring of this unit, and by the simulation of reactions between the effluent and materials beneath the unit by the application of a geochemical model.

2.0 REGULATORY BACKGROUND

The *Hanford Federal Facility Agreement and Consent Order* (Tri-Party Agreement) requires that demonstration of clean closure of a TSD unit must "include documentation that groundwater and soils have not been adversely impacted by the TSD group/unit, as described in 173-303-645 WAC" (Ecology et al., 1996, Section 6.3.1). Because these ponds are surface impoundments, compliance with final status groundwater monitoring (WAC 173-303-645) and a determination of no impact to the groundwater from the unit must be demonstrated to achieve clean closure, in accordance with WAC 173-303-610(2)(b) and Section II.K.1 of the Hanford Facility *Resource Conservation and Recovery Act* (RCRA) Permit. These regulations require cleanup to *Model Toxics Control Act* (MTCA) B levels. It is the intent of this document to demonstrate compliance with these requirements.

In addition to demonstrating that groundwater has not been adversely affected by waste disposal activities at 100-D Ponds, this document will provide evidence that subsurface soils were not contaminated by discharges to the ponds. Demonstration of this will rely on near-surface data and geochemical modeling of the vadose zone and saturated zone. Although clean subsoil is a prerequisite for clean closure of a TSD unit, there is no Washington State Department of Ecology (Ecology) regulation or guidance that requires testing of subsurface soils. The recent clean closure of 2101-M Pond, a RCRA TSD unit, was accepted by Ecology without deep vadose zone data (DOE-RL, 1995).

3.0 DESCRIPTION OF UNIT AND WASTE CHARACTERISTICS

The 100-D Ponds TSD unit is located adjacent to and north of the north perimeter fence of the 100-D Area (Figure 1). Beginning in 1950, before the operation of this site as a TSD unit, this location served as the 188-D Ash Disposal Basin (waste site 126-D-1), which received coal ash from the 184-D Powerhouse. Until 1966, when the ash basin was retired, the location received ash/water effluent only. Between 1966 and 1977 the site received no discharges. Figure 2 is a cross section through 100-D Ponds showing the topographic profile along a northwest-southeast transect and subsurface features, including approximate boundaries of the coal ash and position of the water table.

reacted with the vadose zone in two steps, as described in Section 6.2.2.1. Reaction with ash materials resulted in precipitation of a small amount of barium arsenate, Ca-nontronite (a member of the smectite group of clay minerals), hematite, and sepiolite (a member of the palygorskite group of clay minerals). The minerals anhydrite, portlandite, and quartz reacted with the solution to form the precipitates. The composition of the solution and mass of precipitates and reactants are listed in Table 3.

The calculated pH of the vadose zone solution in equilibrium with coal ash phases is 12.3. The portlandite, a hydrous lime mineral, is responsible for the high pH. The model inputs were varied to determine the influence of small amounts of portlandite in the system, simulating a situation where preferred pathways through the coal ash were used for transport from the surface to the water table and reactive surfaces of portlandite are neutralized. The qualitative result is that only a small amount of portlandite in the system is necessary to increase pH above 12.

The water-ash solution was then equilibrated with minerals typical of the Ringold Formation. This resulted in albite, calcite, and montmorillonite reacting to precipitate anorthite and quartz, with no change in pH of the solution.

The solution produced by reaction with vadose zone minerals was then mixed with groundwater at a ratio of 10% meteoric water to 90% groundwater. This mixing and precipitation of plagioclase, calcite, and montmorillonite reduced the pH to 9.7. Barium arsenate and lead hydroxide are also identified as supersaturated phases in PHREEQC, although the amounts of precipitate are very small (Table 3). Small amounts of hematite, quartz, and boehmite were consumed in this reaction.

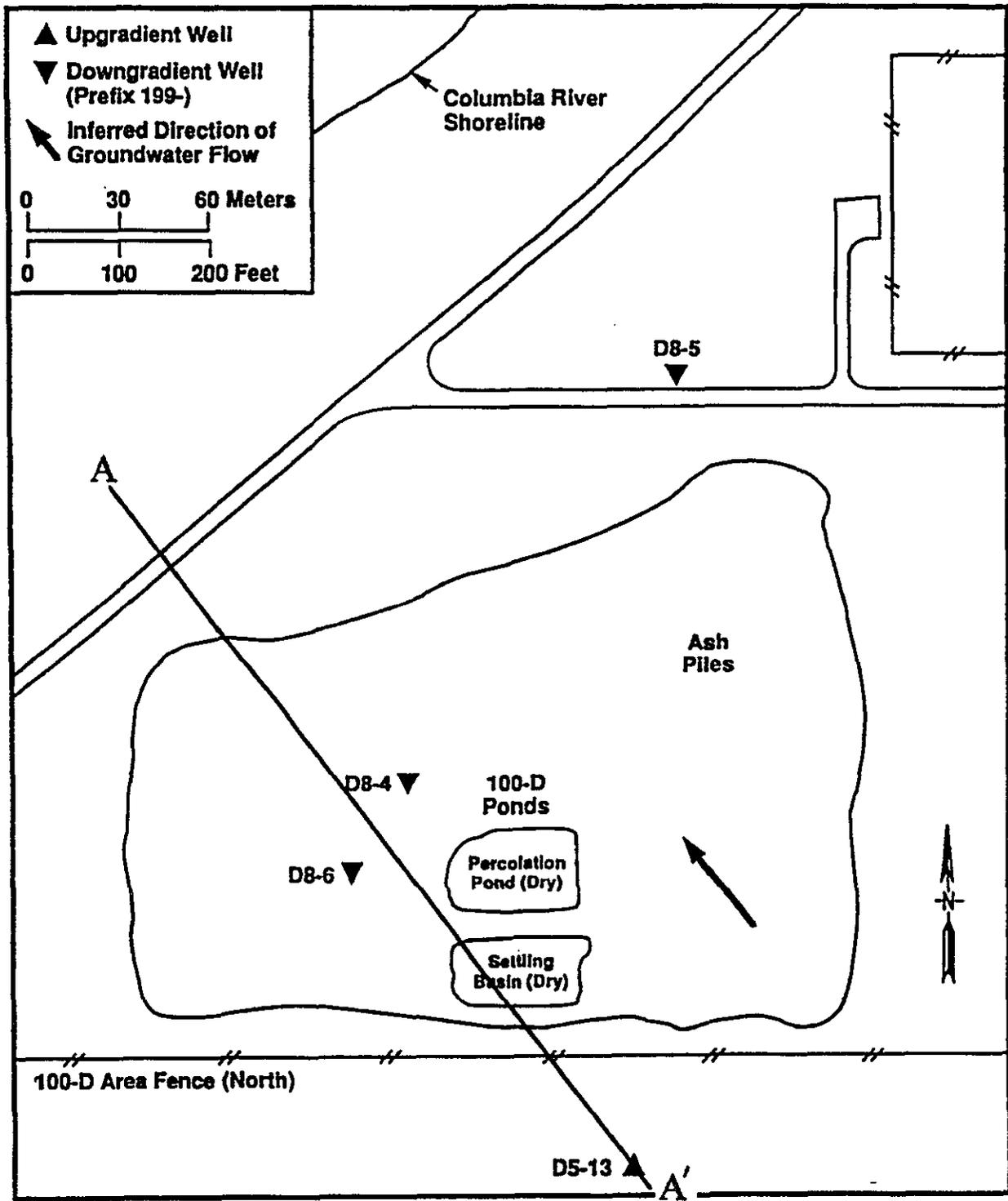
7.0 CONCLUSIONS

The 100-D Ponds received effluent from several different sources in the 100-D Area. The WTF was the source of the greatest volume of effluent, which contained flocculent and sediment entrained in Columbia River water. The MDL contributed a much smaller volume of contaminants but was the likely source of contaminants such as PCBs, although discharge of these and other chemicals has not been documented.

Data from over 5 years of groundwater monitoring clearly demonstrate that operation of 100-D Ponds has not had an adverse effect on groundwater. None of the COCs associated with sediment in the Ponds are elevated in groundwater, and most analyses of COCs from the downgradient wells are below detection limit. Table 1 shows that levels for all COCs are below MTCA B groundwater standards.

Elevated pH values have been recently recorded in two of the three downgradient wells (Hartman, 1996). These two wells have historically had higher pH values than the upgradient wells, which is ascribed to the alkaline characteristics of the coal ash underlying and surrounding the Ponds. The recent increase in pH in the downgradient wells is probably related to cessation of discharge to the

Figure 1. Location of 100-D Ponds and Monitoring Wells. Line marked A-A' is transect for cross section in Figure 2.



2. React the solution derived in step 1 with minerals typical of the Ringold Formation
3. Mix this solution with groundwater, maintaining equilibrium with the Ringold Formation.

The initial solution composition and coal ash composition were selected without precise knowledge of their properties. Ideally, the infiltrating water would be defined by some average or upper statistical bound of the effluent composition released into 100-D Ponds. This information is not available, so the actual composition used was a combination of average Columbia River water for the major elements (PNL, 1994) and the average of TCLP analyses performed on the sediments at the bottom of the settling pond for the metals (BHL, 1995). The Columbia River is a likely primary water source, as approximately 25 million gallons of Columbia River water were received from the WTF during operation of the Ponds. The rationale for using TCLP analyses for metals is that the maximum concentration of metals in infiltrating water would be the leachate from the contaminated sediments; TCLP analyses represent the "worst case" leachate likely to be produced from a sample.

Reaction of a solution with a solid requires the mineral phases of the solid to be known. Lacking mineral analyses of the coal ash, appropriate phases were chosen from published tables of mineral constituents in ash from various coals (Falcone and Schobert, 1986). The minerals anhydrite (CaSO_4), quartz (SiO_2), and hematite (Fe_2O_3) were used to represent the coal ash in the PHREEQC program. In addition, calcium hydroxide in the form of portlandite ($\text{Ca}(\text{OH})_2$) was included as a mineral phase in the ash because high calcium contents are typical of subbituminous coal (Huffman and Huggins, 1986), which was the type used at Hanford.

The solution resulting from reaction of the infiltrating water with coal ash was then reacted with minerals typical of the Ringold Formation. These include quartz, plagioclase feldspar, calcite, and montmorillonite.

The third step was performed to determine if precipitation of any mineral phases was likely to occur when the reacted water was mixed with groundwater. The groundwater chosen was an average of pre-1994 analyses from the upgradient monitoring well, 199-D5-13. The restriction on the date was necessary because this well started to become contaminated with chromium and other constituents (Figure 3) from upgradient sources in 1995, due to dissipation of the groundwater mound beneath the Ponds as discharges diminished and finally ceased in June, 1994.

6.2.2.2 Results of Modeling. The model PHREEQC was run with the above inputs. The output produced by the program contains the composition of the modeled solution after each step, the distribution of the various aqueous species, and the saturation index of all minerals in the thermodynamic database that contain the components considered in the aqueous and solid phases. Phases that are in equilibrium with the solution have a saturation index equal to 0. Phases with a saturation index greater than 0 indicate that they are thermodynamically oversaturated and may precipitate from solution. After each reaction step, those phases with a saturation index greater than 0 were evaluated and allowed to precipitate if they were geologically feasible.

The first step in the modeling procedure was speciating the initial solution, which is Columbia River water with metals from TCLP analysis of the sediments added to it. This solution was then

Figure 2. Cross Section Through 100-D Ponds. See Figure 1 for transect location. Patterned area is inferred extent of coal ash. All measurements in meters.

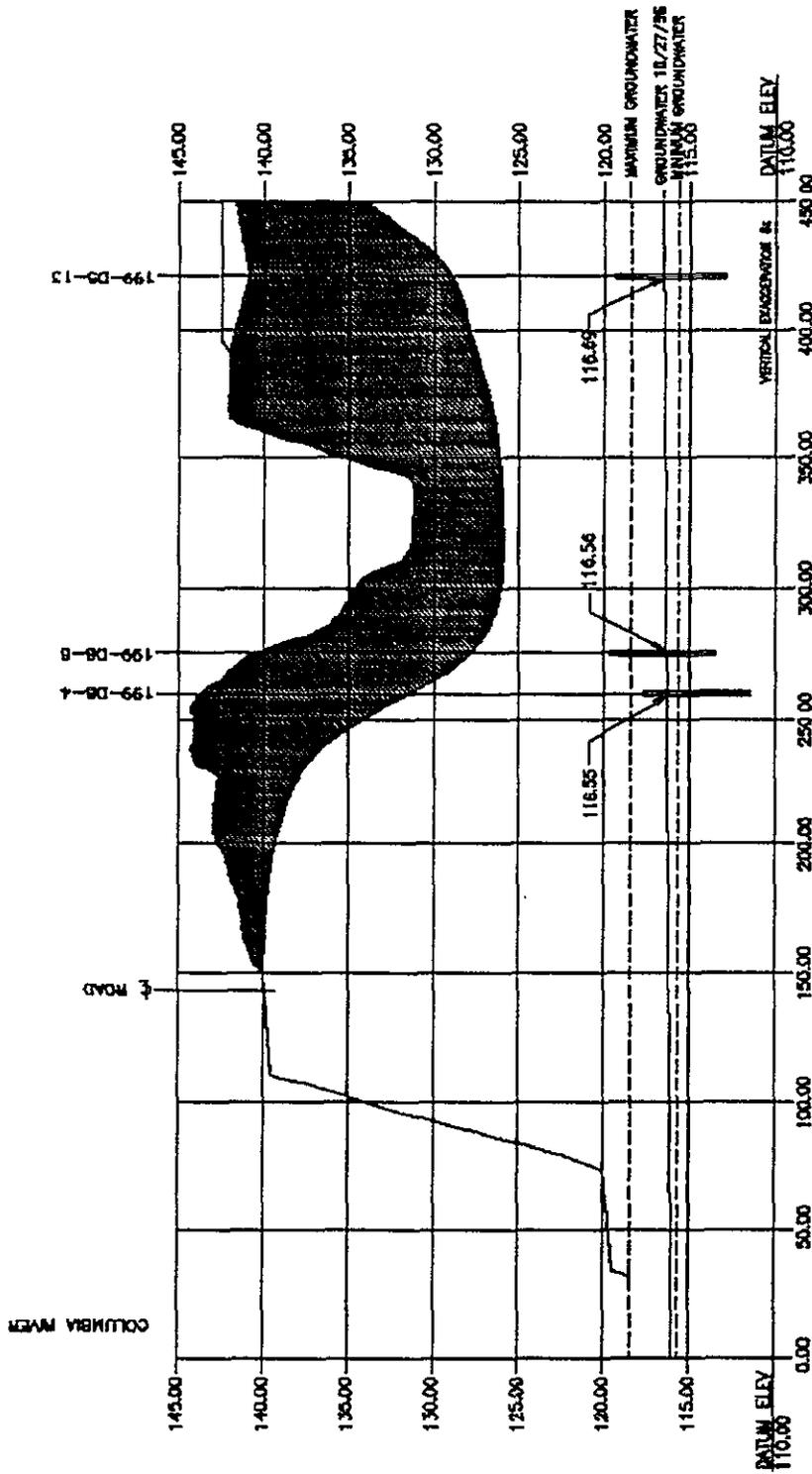


Table 2. Summary Statistics and Compliance with Cleanup Limits for August, 1996, Verification Data. The statistics are computed on 16 samples. All units in mg/kg.

Ecology Test	Aroclor-1254	Aroclor-1260	Ag	As	Ba	Be
Distribution	Below detection	Below detection	Lognormal	Nonparametric	Lognormal	Nonparametric
Value used for compliance	maximum	maximum	lognormal 95% UCL	maximum	lognormal 95% UCL	maximum
Compliance value	0.07	0.04	0.76	4.20	127.80	0.63
Cleanup Limit	0.13	0.13	5	6.47	5600	1.51
Is compliance value > CL?	YES	NO	NO	NO	NO	NO
Datum > 2X CL?	NO	NO	NO	NO	NO	NO
> 10% of data > CL?	NO	NO	NO	NO	NO	NO
Summary Statistics						
% data below DL	93.75	100	0	0	0	0
95% UCL on mean	NA	NA	0.76	1.44	127.80	0.58
Minimum	0.033	0.033	0.47	0.41	74.1	0.39
Maximum	0.072	0.036	0.96	4.2	166	0.63
	Cd	total Cr	Cr⁶⁺	Cu	Hg	Mn
Distribution	Lognormal	Nonparametric	Below detection	Lognormal	Below detection	Lognormal
Value used for compliance	lognormal 95% UCL	nonparametric 95% UC	maximum	lognormal 95% UCL	maximum	lognormal 95% UCL
Compliance value	1.30	7.98	0.62	13.20	5.30	326.34
Cleanup Limit	80	18.5	8	59.2	24	11200
Is compliance value > CL?	NO	NO	NO	NO	NO	NO
Datum > 2X CL?	NO	NO	NO	NO	NO	NO
> 10% of data > CL?	NO	NO	NO	NO	NO	NO
Summary Statistics						
% data below DL	0	0	87.5	0	68.75	0
95% UCL on mean	1.30	7.98	NA	13.20	NA	326.34
Minimum	0.95	3	0.56	10.85	0.02	266
Maximum	1.5	22.5	0.62	16	5.3	362
	Ni	Pb	Sb	Tl	V	Zn
Distribution	Nonparametric	Nonparametric	Below detection	Below detection	Nonparametric	Nonparametric
Value used for compliance	maximum	maximum	maximum	maximum	maximum	maximum
Compliance value	19.30	6.40	5.40	0.19	73.15	93.60
Cleanup Limit	32	250	10	2	85.1	24000
Is compliance value > CL?	NO	NO	NO	NO	NO	NO
Datum > 2X CL?	NO	NO	NO	NO	NO	NO
> 10% of data > CL?	NO	NO	NO	NO	NO	NO
Summary Statistics						
% data below DL	0	0	81.25	0	0	0
95% UCL on mean	10.07	2.96	NA	NA	69.08	57.35
Minimum	6.6	1.25	3.5	0.11	39.1	37.4
Maximum	19.3	6.4	5.4	0.19	73.2	93.6

PHREEQC invokes a separate database file for the requisite thermodynamic data on the components, species, and phases necessary to perform the calculations. The database used for this modeling effort was adopted from the program MINTEQA2, which has a comprehensive list over 1,100 species and more than 500 phases.

6.2.2.1 Methodology. The modeling parameters were formulated to mimic the reactions that would be expected to occur beneath 100-D Ponds. PHREEQC allows several steps to be performed in one run; the resulting output gives the results of each step and the final result of the run. For 100-D Ponds, the various steps were as follows:

1. React infiltrating water with coal ash underlying the Ponds

The 100-D Ponds TSD unit was constructed as a surface impoundment for liquid effluent and operated between 1977 and 1994. It was constructed primarily for the impoundment and disposal of nonradioactive, nondangerous liquid effluent from the 183-D Water Treatment Facility (WTF). Constituents that may have been discharged to 100-D Ponds include the following:

1. **Corrosive Chemicals.** Until 1986, the 189D Method Development Laboratory (MDL) occasionally discharged potentially corrosive effluents from the regeneration of three demineralizers to the process sewer system, which in turn emptied into the 100-D Ponds. These effluents may have exhibited pH levels below 2.0 or above 12.5 upon arrival at the ponds, although their actual corrosivity level was never established. It is the potential for this site to have received these corrosive chemicals that led to the classification of the 100-D Ponds as a TSD unit.
2. **Mercury.** No records exist that identify disposal of mercury into 100-D Ponds; however, the presence of liquid metallic mercury was visibly confirmed in the floor drain of the 189-D Building mechanical development laboratory in 1989 (Price, 1989). Gano and Lauterbach (1990) documented that accidents involving laboratory instruments such as manometers and mercury switches could have contributed up to 2.6 kilograms (5 pounds) of mercury to the process sewer system (Gano and Lauterbach, 1990). It is unlikely that a significant portion of this mercury could have been deposited in the ponds, as mercury traps were installed 3 years before the ponds began receiving effluent in 1977 and considerable flushing of the system would have occurred before that time.
3. **Dangerous Shop Chemicals.** Until 1988, when the 189D MDL was permanently closed, standard volatile organic shop chemicals such as thinners and solvents could have been released to the 100-D Ponds from open floor and sink drains of the craft shop or the mechanical development laboratory of the 189D MDL complex. However, such chemicals were not normally stored in bulk quantities nor were they procedurally discharged to the drain system when spent.
4. **Radioactive Constituents.** Unirradiated uranium fuel elements used during testing at the Fuel Discharge Trampoline Test Facility may have contributed radiological contamination to 100-D Ponds. A discussion of radionuclides at the ponds is presented here for information only, because these constituents are outside the scope of WAC 173-303.
5. **Concentration of Naturally Occurring Metals from Columbia River Water and Sediment.** The filters used at the 183-D WTF removed suspended and colloidal minerals from the river water, which would have been discharged into the 100-D Ponds during periodic backflushing of the filters. Semi-annual washdowns of the 183-D water storage basins also discharged river sediment and flocculent into the 100-D Ponds along with Columbia River water.

3.1 CONTAMINANTS DEPOSITED IN 100-D PONDS

Two different sampling and analysis efforts have been conducted to characterize the ponds, one in August, 1992 and the other in January, 1995 (BHL, 1995). Samples were analyzed for metals and

Additional samples were collected from the bottom of the ponds after removal of the contaminated sediments in August, 1996. Data from these samples, summarized in Table 2, are below Ecology MTCA B cleanup standards, indicating that contamination was fixed in the fine-grained sediments and did not migrate into the vadose zone.

6.2 MODELING OF SUBSURFACE SOIL

In order to evaluate the possibility that dangerous wastes or dangerous waste constituents have migrated and been deposited into the vadose zone, geochemical modeling was performed to simulate reactions between infiltrating water and the various sediment types that occur beneath 100-D Ponds. The computer code PHREEQC was used for this simulation to identify the composition of solutions reacting with subsurface mineral assemblages and identify any phases that may precipitate. PHREEQC is distributed and maintained by the U.S. Geological Survey.

6.2.1 The Computer Program PHREEQC

The computer code PHREEQC is based on an ion-association aqueous model with capabilities for speciation and saturation-index calculations, and other calculations involving mixing of solutions, mineral and gas equilibria, and ion-exchange reactions. The model uses thermodynamic data to simulate equilibrium conditions between different phases. A manual detailing the theory and operation of this program is available (Parkhurst, 1995). This program and its precursor, PHREEQE, have been used for over 15 years for modeling surface and subsurface aqueous geochemical reactions.

6.2.2 Application of PHREEQC to 100-D Ponds

The computer model PHREEQC calculates geochemical conditions at *equilibrium*, which necessitates the assumption that water-rock contact time is adequate to achieve equilibrium conditions. This was probably not the case during much of the time the ponds were active as an effluent disposal facility, because large amounts of water were discharged in a short time period and quickly reached the groundwater table. Evidence of this can be seen from a January, 1993 incident where 1,136,000 liters (300,000 gallons) of water from the settling basins were inadvertently emptied into 100-D Ponds (Alexander, 1993). A rise of several centimeters was measured in most of the monitoring wells within several days of this discharge, indicating fast infiltration rates and thus little time for equilibration to occur.

After discharges to the ponds ceased in June, 1994, recharge to the vadose zone beneath the ponds effectively ceased and travel time for residual vadose zone waters increased. This residual water had longer to react with the ash and Ringold Formation and was more likely to be at equilibrium with the solid phases. The assumption of equilibrium should yield the most dissolution and precipitation and thus represents a "worst case" situation.

organic analytes using both total (SW-846) and toxic characteristic leaching procedure (TCLP) analytical preparation and analysis techniques. Samples of the coal ash surrounding the ponds were also collected in September, 1992.

Characterization data indicated that some contaminants were present in the sediment on the bottom of the settling pond. These constituents probably originated from the 189D MDL complex and arrived by way of the process sewer system. Constituents that were present above Ecology's MTCA B levels include polychlorinated biphenyls (PCBs), arsenic, barium, cadmium, chromium, copper, lead, mercury, nickel, vanadium, and zinc. The coal ash underlying the sediment has no significant contamination; all levels for contaminants of concern (COCs) are below MTCA B limits.

The contaminated sediments, which consisted of naturally occurring fine-grained material and alum (discussed in Section 4.1), were removed and disposed of in August, 1996. The floors of the settling and percolation ponds were sampled shortly after this remediation. Data from these samples are presented and discussed in Section 6.0.

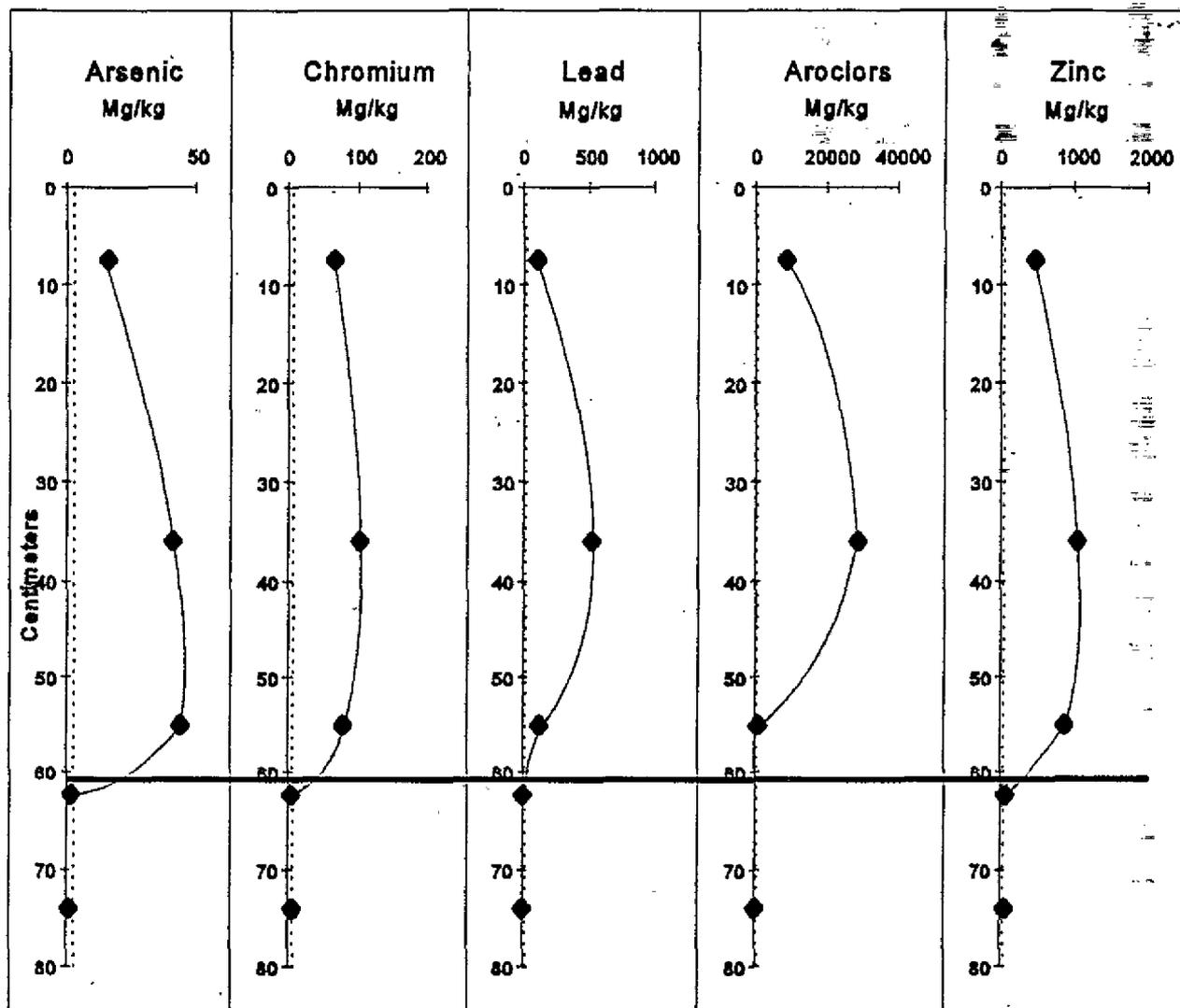
4.0 PHYSICAL AND CHEMICAL FACTORS AFFECTING CONTAMINANT MIGRATION

The effluent discharged to 100-D Ponds was predominantly water from the 183-D WTF. As discussed in Section 3.0, some corrosive liquids and miscellaneous chemicals were also discharged through the process sewer system into the ponds, along with river sediment and flocculent used in the water treatment process. These latter solids are important to consider when evaluating the mobility of metals and PCBs, as fine-grained sediment and flocculent have the ability to adsorb many chemicals and effectively immobilize them in an aqueous environment. It is thus possible that chemicals discharged into the ponds were fixed in the upper layer of sediment composed of flocculent and solids filtered from Columbia River water. A discussion of the use of flocculents for binding contaminants in water follows.

4.1 FLOCCULENTS IN WATER TREATMENT

Coagulants and flocculents are used in liquid/solids separation applications to neutralize the ionic charges that surround solid particles dispersed in water, and cluster them together to promote settling. Most naturally occurring particles have a negatively charged surface in water due to the release of cations such as Na^+ and Ca^{2+} from the surface of the particle into the surrounding water. When microscopic particles of like charge approach one another, they repel and cannot coalesce to form larger particles. This leads to very stable systems of particles in water that will not settle. Cationic coagulants adsorb onto the negatively charged particle surfaces and neutralize the negative charges that are causing repulsion. Optimum coagulation occurs when the particle surface charge is reduced to near zero.

Figure 4. Concentration Profile of Several Constituents in 100-D Ponds Sediment and Underlying Ash (below dark horizontal line). Dashed line is average of "background" coal ash samples surrounding and underlying 100-D Ponds.



The agent used at the 183-D WTF as a coagulant and flocculent was aluminum sulfate (alum). This compound and others like it (e.g., ferric chloride) have trivalent metal ions (Al^{+3} and Fe^{+3}) that are strongly attracted to any negatively charged surface. Trivalent cations are desirable coagulants when compared to divalent and monovalent cations, which have very weak coagulating abilities. The use of alum usually produces a fairly clean supernatant water since the metal hydroxides produced assist in the capture of very fine particles. Use of alum also tends to lower the pH of the system as anions are adsorbed.

The flocculent released into the ponds would carry with it the contaminants (natural or anthropogenic) adsorbed at the WTF, but would also probably have excess adsorption capacity when it was deposited on the surface of the settling pond. It is therefore likely that this alum would bind much of the contamination entering with the liquid effluent and prevent contaminants from migrating through the vadose zone. Data supporting this postulate are presented in Section 6.0.

5.0 EVALUATION OF GROUNDWATER DATA

Groundwater monitoring at 100-D Ponds began in 1992. As required by 40 CFR 265.92, groundwater is analyzed for groundwater quality parameters, drinking water parameters, and contamination indicator parameters. Statistical comparisons of contamination indicator parameters upgradient and downgradient of the site are made on a quarterly basis. This phase of groundwater monitoring is commonly called "indicator evaluation" or "detection" monitoring.

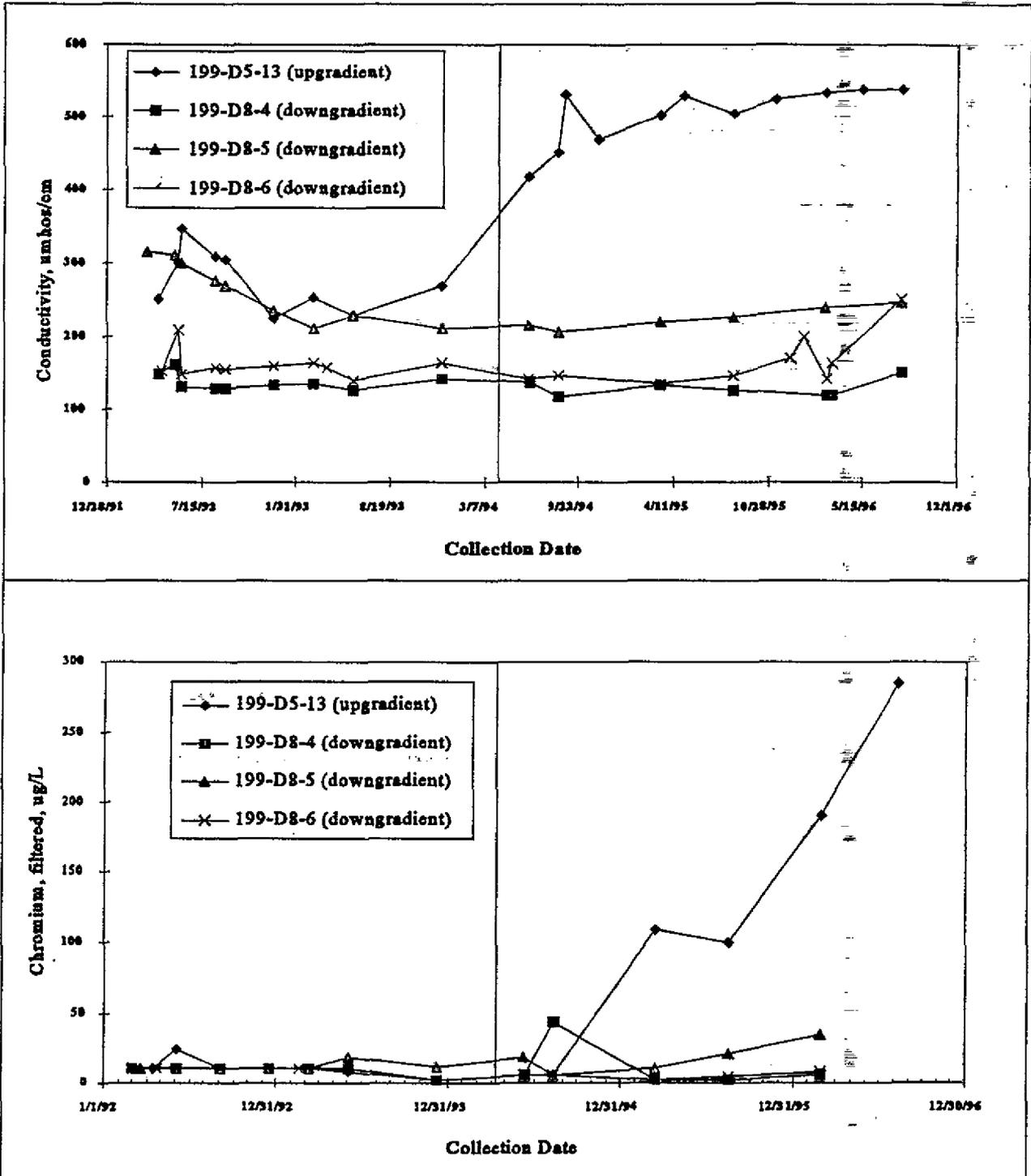
The groundwater monitoring network for the 100-D Ponds is composed of one upgradient and three downgradient wells (Figure 1). The wells are completed at the top of the unconfined aquifer.

5.1 GROUNDWATER QUALITY

Four quarters of data were collected in 1992 and 1993 and analyzed for a complete suite of organic and inorganic constituents and radionuclides. These constituents are listed in Appendix A and are compared to the groundwater monitoring analytes listed in 40 CFR 264, Appendix IX; this suite of analytes is far more extensive than required by regulations addressing interim status groundwater monitoring. Quarterly samples collected since 1993 have been analyzed for a suite of metals, anions, field measurements, and radiological components. A summary of the types of analyses performed for each sampling event is presented in Appendix A.

Table 1 contains a statistical summary for contaminants of potential concern from the three downgradient wells and shows that their concentrations in groundwater are below MTCA B groundwater cleanup standards. Of special concern are the chemicals that were found to be above MTCA B soil cleanup standards in the sediments of the settling pond, namely PCBs,

Figure 3. Conductivity and Chromium Values from 100-D Ponds Monitoring Wells from December, 1991 to December, 1996.
Vertical line represents end of discharges to the Ponds.



**Table 1. Statistical Summary of Groundwater Samples from Monitoring Wells
Downgradient of 100-D Ponds.**

Compound	Filtered/ Unfiltered	Average	Std. Dev.	Min	Max	# Samples	# Samples		MTCA B GW	Max value > MTCA B?
							<DL	% > DL		
Antimony	Filtered	60.73	41.47	12	100	37	37	0		NA
Aroclor-1016	Unfiltered	0.50	0.00	0.5	0.5	12	12	0	1.12	NO
Aroclor-1221	Unfiltered	0.63	0.23	0.5	1	12	12	0		NA
Aroclor-1232	Unfiltered	0.50	0.00	0.5	0.5	12	12	0		NA
Aroclor-1242	Unfiltered	0.50	0.00	0.5	0.5	12	12	0		NA
Aroclor-1248	Unfiltered	0.50	0.00	0.5	0.5	12	12	0		NA
Aroclor-1254	Unfiltered	0.50	0.00	0.5	0.5	12	12	0	0.32	YES (DL)
Aroclor-1260	Unfiltered	0.50	0.00	0.5	0.5	12	12	0	0.011	YES (DL)
Arsenic	Filtered	2.42	0.19	2	2.5	19	16	16	4.8	NO
Barium	Filtered	25.28	15.42	10	70	37	7	81	1120	NO
Beryllium	Filtered	1.04	0.53	0.085	1.5	37	34	8	80	NO
Cadmium	Filtered	3.38	1.75	0.49	5	37	33	11	8	NO
Chromium	Filtered	10.54	8.24	1.85	44	37	27	27	80	NO
Copper	Filtered	6.16	4.21	1.05	10	37	34	8	592	NO
Lead	Filtered	2.58	0.34	2.5	4	19	18	5	5	NO
Manganese	Filtered	5.26	10.43	0.275	63	37	22	41		NA
Mercury	Filtered	0.07	0.03	0.0095	0.1	37	34	8	4.8	NO
Nickel	Filtered	12.06	6.50	5.5	42	37	36	3	320	NO
Silver	Filtered	6.12	4.06	1.435	10	37	37	0	80	NO
Vanadium	Filtered	10.45	5.21	1.92	15	37	26	30	112	NO
Zinc	Filtered	4.97	2.60	1.3	13	37	24	35	4800	NO

NA = not applicable

(DL) = Detection limit for analyte above regulatory limit.

arsenic, barium, cadmium, chromium, copper, lead, mercury, nickel, vanadium, and zinc. None of these constituents were found in the downgradient wells at levels that would indicate contribution from 100-D Ponds. These results indicate that effluent disposal activities at 100-D Ponds did not have any adverse effects on groundwater.

Although discharges to 100-D Ponds did not create a groundwater mound detectable by water levels in the monitoring wells, the effect of the discharges can be seen in the water chemistry data. The greatest volume of effluent routed to the Ponds was raw or treated river water released from the 183-D WTF, which would result in dilution of the groundwater beneath the Ponds. Upgradient of 100-D Ponds, the groundwater is contaminated with chromium, tritium, and nitrate, while downgradient wells show concentrations of these constituents are diluted to values typical of or below background concentrations for the Hanford Site (DOE-RL, 1996a) by discharges into 100-D Ponds.

Figure 3 shows chromium concentrations and conductivity measurements over time for the upgradient and downgradient monitoring wells. These plots show that water quality in the upgradient wells has degraded since the decrease of discharges to 100-D Ponds and final cessation in May, 1994, while concentrations in the downgradient wells have changed little since that time. This is interpreted to be the result of the lack of "clean" water from past discharges to dilute the contaminated water entering the area from upgradient sources.

The RCRA groundwater monitoring program for interim status units (40 CFR 265, Subpart F) requires a comparison of concentrations of various indicator parameters from downgradient wells with critical mean values calculated from an upgradient well. Over the course of groundwater monitoring at 100-D Ponds, pH is the only parameter that has exceeded the critical value. This exceedence occurred in February, 1996 in the two downgradient wells 199-D8-4 and 199-D8-6. Ecology was notified of this exceedence, and an assessment report was submitted (Hartman, 1996). It was concluded that the coal ash underlying the Ponds is the source of the elevated pH in the groundwater.

6.0 EVALUATION OF SUBSURFACE SOILS

In order to clean close a TSD unit, it must be demonstrated that "... levels of dangerous waste or dangerous waste constituents or residues do not exceed ... MTCA B ..." [WAC 173-303-610(2)(a)]. Data from near-surface soil samples (discussed in Section 6.1) and from groundwater analyses (Section 5.1) show no evidence that contaminants found in the surface sediments of 100-D Ponds migrated into the vadose zone and groundwater system. This premise is investigated in this section, by evaluating near-surface soil samples and applying a geochemical model to investigate subsurface reactions between infiltrating solutions from 100-D Ponds and vadose and saturated zone materials.

6.1 DATA FROM NEAR-SURFACE SAMPLES

Data collected in the 1995 characterization effort (Phase II) were from surface samples and various depths, collected from four different test pits with a maximum depth of 2.4 m (8.0 ft). These data and analyses of the 1992 samples (Phase I) were used in the decision to remediate this TSD unit by removing the sediment from the settling pond. The Phase II data show that the contaminants are restricted to the fine-grained sediment in the settling pond. These contaminants include PCBs, arsenic, chromium, and lead, among others (DOE-RL, 1996b). The Phase II data also show that the concentrations of these contaminants drop sharply in the ash underlying the sediment. Figure 4 shows this relationship for several contaminants.

Several samples intended to characterize the background composition of the coal ash surrounding and underlying 100-D Ponds were also collected in 1992. Average compositions for these samples are included in Figure 4, and show that the materials underlying the sediment in Phase II samples are similar in composition to the background coal ash samples.