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7. Abstract

This document presents the results of laboratory and field investigations conducted in FY 1993 and FY 1994 to determine chromium speciation and transport characteristics in the 100-D and 100-H Areas of the Hanford Site. Analyses of groundwater and seep water samples indicate that dissolved chromium is primarily in the hexavalent oxidation state. Sediment characterization activities suggest that a minor portion of chromium may be reduced and precipitated on riverbank sediments as groundwater passes through the river/aquifer interfacial zone. Laboratory mixing tests conducted with chromate-contaminated groundwater and Columbia River water suggest that Cr(VI) remains primarily in the hexavalent oxidation state after entering the Columbia River, with total chromium concentration values decreasing in proportion to the degree of dilution.

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EXECUTIVE SUMMARY

This report presents the results of a field and laboratory investigation conducted to define the fate and transport characteristics of chromium in the 100D/H Areas of the Hanford Site. This work was undertaken to provide information relevant to assessing the potential for release of hexavalent chromium to the Columbia River from the Hanford Site. Included in this study was the determination of the concentration and aqueous speciation of chromium in the unconfined aquifer, and an assessment of potential changes in speciation as groundwater flows through the river/aquifer transition zone and mixes with the Columbia River.

The following three approaches were utilized in the course of this study to define the fate of chromium:

- Determination of chromium speciation of water samples
- Characterization studies involving riverbank sediments
- Mixing tests involving Cr-contaminated groundwater with river water.

In addition, groundwater chromium plume maps have been constructed using existing monitoring data from the 100-D and 100-H Areas. This and related information is useful in placing the data from this study in a hydrogeologic context.

Samples of groundwater, seep water, and Columbia River water were collected for the chromium speciation studies. These samples were analyzed by standard EPA methods for cations, metals, and anions. Total and trivalent/hexavalent determinations were also performed by several approaches. Results indicate that most of the dissolved chromium in the groundwater, seep water, and river water samples is in the hexavalent state. This is consistent with the known aqueous chemistry of chromium. In particular, elevated concentrations of hexavalent chromium (>30 ppb to as high as 140 ppb) were measured in several of the seeps of the 100-D and 100-H Areas.

Sediments were also collected along the edge of the Columbia River in the vicinity of the 100-D Area seeps. These samples were characterized by sequential extraction and batch sediment/solution interaction tests to evaluate the potential for uptake of chromium by sediments. The sequential extraction tests indicate that the sediment samples contain chromium at concentrations somewhat higher than normal background values, suggesting that uptake of chromium occurs as groundwater passes through the riverbed. The partitioning of the chromium was determined to be primarily in an oxide phase, suggesting that the uptake mechanism involves reduction of hexavalent in pore fluids and precipitation as Cr(III) hydroxide on soil grain surfaces. The batch tests involved exposure of the sediments to solutions containing Cr(III) and Cr(VI). During these tests, some hexavalent chromium was observed to appear in the solutions followed by a declining concentration of trivalent and hexavalent chromium. These results are interpreted to suggest that a minor amount of Cr(III) can be oxidized to Cr(VI) by the sediments owing to the presence of manganese oxide components. The dominant tendency, however, is

for chromium to be reduced by labile ferrous iron and organic matter in the sediment.

It is concluded that riverbed sediments tend to reduce and precipitate hexavalent chromium from groundwater passing through them, thus resulting in the reduction of a portion of the dissolved chromium from the hexavalent to the nontoxic, immobile trivalent oxidation state. The proportion of chromium removed from the aqueous phase by this process is relatively insignificant, however, owing to the limited capacity for uptake of chromium by the sediments. This conclusion is supported by the chemistry associated with pore water samples collected from sediments near the river using a drive point. A direct correlation between Cr(VI) concentrations and fluid conductivity was observed for these samples, suggesting a simple mixing model involving groundwater and river water that reflects a predominantly conservative chemical behavior for Cr(VI) in this environment.

Mixing studies were also conducted that involved combining various ratios of Cr-contaminated groundwater and river water. The objective of these tests was to determine if the speciation of chromium changes as chromium-contaminated groundwater discharges into the Columbia River. Very little change was seen in the concentration of hexavalent chromium with time in these tests, although a slight decline was observed at the higher ratios of river water to groundwater. These results indicate that river water does not have a significant reduction capacity. It is concluded that hexavalent chromium introduced into the Columbia River behaves essentially as a conservative constituent. That is, chromium concentration values decrease in proportion to the extent of dilution, and chromium tends to remain in the hexavalent oxidation state during mixing with river water. After significant dilution, however, a portion of the hexavalent chromium will probably be reduced and precipitated by reaction with particulates within the water column.

The results of this study demonstrate that chromium present within the Hanford unconfined aquifer of the 100-D and 100-H Areas is predominantly in the hexavalent oxidation state. It is apparently relatively stable in this form, owing to the lack of organic matter within the aquifer. Some of the chromium is removed as the groundwater passes through the river/aquifer transition zone due to reduction and precipitation associated with sediment/water interaction processes. Chemical data collected on seep water samples, however, suggests that most of the hexavalent chromium ultimately discharges into the Columbia River. Dilution of hexavalent chromium subsequently occurs during the mixing of groundwater and river water, with relatively little change taking place in speciation.

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1.0 INTRODUCTION

Elevated chromium concentrations have been consistently reported in the analyses of groundwater samples collected from a number of wells in the 100-D and 100-H Areas of the Hanford Site. In addition, samples collected from springs or seeps at the edge of the Columbia River adjacent to these areas contain elevated concentrations of chromium (DOE-RL, 1992a). It also known that hexavalent chromium is present in the groundwater of the 100-H Area and seeps adjacent to the Columbia River (Peterson and Johnson, 1992). The speciation of the chromium in the groundwater or the seep water has not been determined in a quantitative manner to date, however.

This report presents the results of field and laboratory activities conducted to determine the state of speciation of chromium in groundwater, seep water, and Columbia River water in and adjacent of the 100-D and 100-H Areas. This work was also conducted to obtain information needed to predict changes in the speciation and transport characteristics of chromium as groundwater flushes through riverbank and riverbed sediments and subsequently mixes with the water column of the Columbia River.

The sampling, characterization, and testing activities described in this report were undertaken to meet the requirements identified in Activity 1A-4 (Chromium Speciation) of DOE-RL (1992b). Activity 1A-4 addresses the need to determine if hexavalent chromium present in groundwater will remain in the hexavalent state upon entering the river column or if it will be reduced to the much less toxic trivalent state. This study also addresses the need identified in Activity 1A-4 to develop sampling techniques and analytical methods for speciating chromium present in groundwater of the 100 Area.

Three major areas of activity were undertaken to accomplish these objectives. The first involved collection of groundwater, seep water, and Columbia River water from the 100-D and 100-H Areas for analysis and determination of chromium speciation. Riverbank sediments were also collected to conduct laboratory studies for the purpose of determining the amount and chemical state of chromium present in the sediments. Information provided by these sediment characterization activities should also serve to identify the mass transfer mechanisms involving distribution of chromium during sediment/water interaction processes occurring in the river/groundwater interfacial zone. Finally, mixing studies were conducted involving several ratios of Cr(VI)-contaminated groundwater and Columbia River water. The primary objective of these mixing tests is to provide information needed to assess changes in concentration and speciation of dissolved chromium that take place as groundwater enters the Columbia River, and the extent of subsequent partitioning of chromium into the suspended particulate fraction or removal by precipitation within the river.

2.0 ENVIRONMENTAL ASPECTS OF CHROMIUM GEOCHEMISTRY

2.1 CHEMISTRY OF CHROMIUM

Chromium commonly occurs in the III and VI oxidation states in terrestrial and marine environments (Adriano 1986, Rai et al. 1989, Richard and Bourg 1991, and WHC 1993a). Chromium is present in minor amounts in igneous rocks, but in higher concentrations in basic and ultrabasic types than in the more silicic rock types. Basaltic igneous rocks contain an average of 220 ppm chromium, granitic igneous rocks average 20 ppm, sandy sediments average 25 ppm, and shales and clays average 120 ppm (NRCC 1976 and Richard and Bourg 1991).

The principal uses of chromium are in the metallurgical, leather tanning, and chemical industries, and as a corrosion inhibitor. Chromium has been utilized at the Hanford Site as an anticorrosion agent in reactor cooling systems (2 mg/L sodium dichromate; Richards 1953) and for decontamination activities.

The chemical state of chromium in the environment is important because hexavalent chromium is more toxic and more mobile than chromium in the trivalent oxidation state (Rai et al. 1989). The primary chemical processes controlling the fate and transport of chromium in the environment are precipitation/dissolution of Cr(III) compounds, hydrolysis of Cr(III), redox transformation of Cr(III)/Cr(VI), and adsorption/desorption of Cr(VI).

Chromium (III) forms strong aqueous hydroxo complexes (i.e., hydrolyzes). Solubility studies of $Cr(OH)_3$ by Rai et al. (1987) indicate that the dominant hydroxo species are $CrOH^{2+}$ at pH values from 3.8 to 6.3, $Cr(OH)_3^{\circ}$ at pH values from 6.3 to 11.5, and $Cr(OH)_4^-$ at pH values >11.5. Cr(III) does not appear to form significant complexes with other common ligands.

The dominant Cr(VI) aqueous species in natural waters are the chromate anions, $HCrO_4^-$ and CrO_4^{2-}. The dichromate anions ($HCr_2O_7^-$ and $Cr_2O_7^{2-}$), while important in industrial applications, are not anticipated to be present at the lower Cr(VI) concentrations generally encountered in the environment ($<10^{-2}$M; Baes and Mesmer 1976). The pK for $HCrO_4^-$ is 6.5 (Stollenwerk and Grove 1985 and Moeller and O'Connor 1972).

The Eh-pH diagram presented in Figure 1 illustrates the dominant fields of stability for the aqueous chromium species. The hydroxo complexes of Cr(III) are stable at medium to low redox potentials and their field of predominance vary with pH, as discussed above. The hexavalent chromate anions are stable only under oxidizing conditions and react with reducing agents to form the trivalent aqueous species or solids. Chromate becomes a stronger oxidizing agent with decreasing pH, as indicated in Figure 1 by the slope of the stability line between the Cr(VI) and Cr(III) species (Hem 1977). Thus, Eary and Rai (1988, 1989) demonstrated that chromate is readily reduced by the ferrous ion and precipitated as $(Cr_xFe_{1-x})(OH)_3$. Cr(VI) can also be reduced in the environment in the presence of organic matter (Schroeder and Lee, 1975; Bartlett and Kimble, 1976; James and Bartlett, 1983; Ross et al. 1981) or hydrogen sulfide gas (Smillie et al. 1981; Thornton et al. 1989).

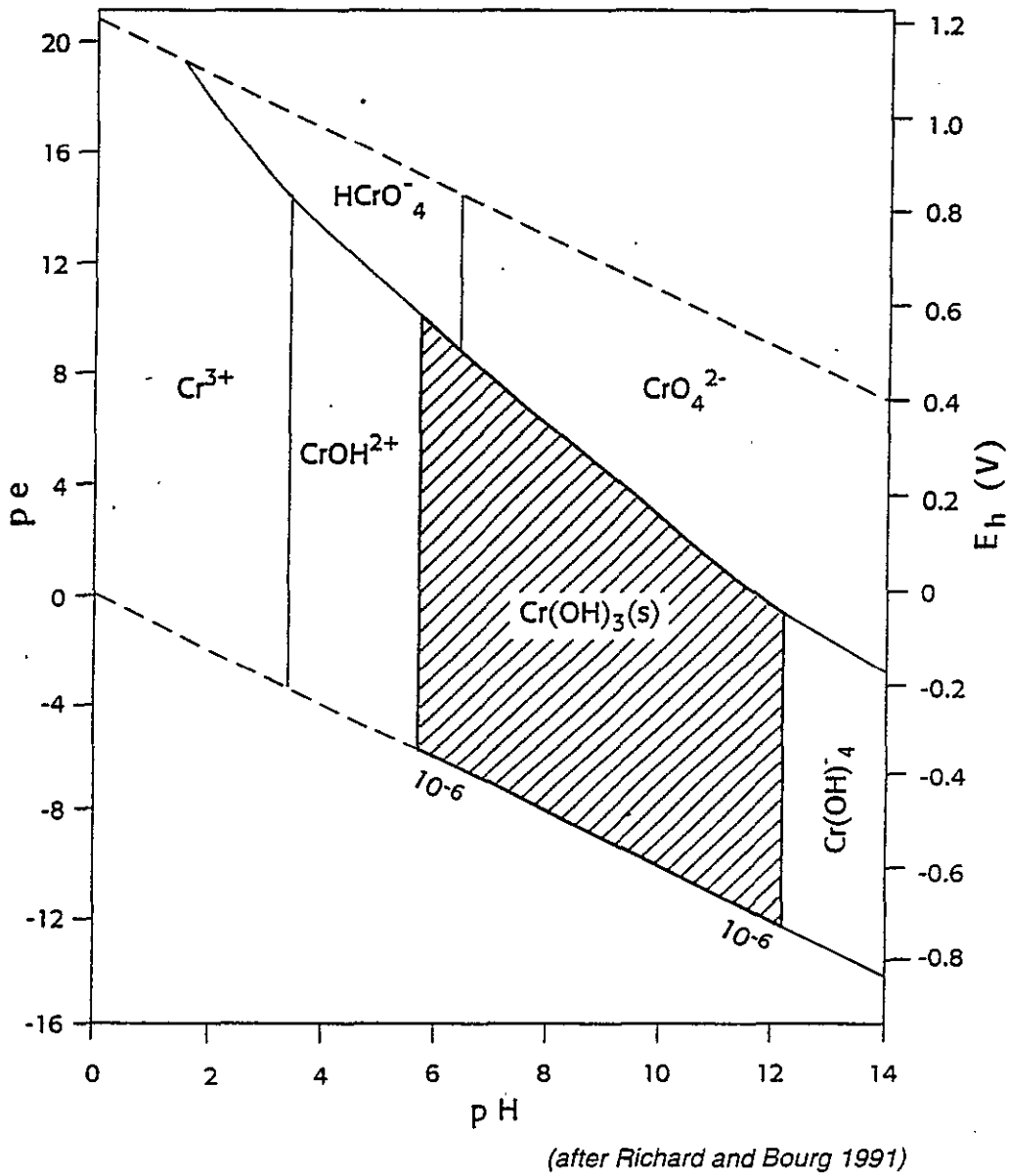

Figure 1. pe-pH Relationships for Dissolved Aqueous Chromium in the Presence of $Cr(OH)_3(s)$. The hatchered zone represents the domain of stability of $Cr(OH)_3(s)$ for 10^{-6}M total dissolved chromium. Diagram constructed using equilibrium data from Rai et al. (1987).

Hexavalent chromium is very soluble under oxidizing conditions, although Rai et al. (1989) suggest that $Ba(S,Cr)O_4$ may be a solubility controlling solid in some soils. Trivalent chromium is relatively insoluble under reducing conditions at neutral to high pH values. Chromium (III) appears to precipitate in low-temperature environments primarily as chromium hydroxide, $Cr(OH)_3$, or mixed iron-chromium oxyhydroxides in systems containing iron (Rai et al. 1987, Sass and Rai 1987, and Eary and Rai 1988 and 1989). Thus, reduction of hexavalent chromium to trivalent chromium will generally result in precipitation of the chromium as a hydroxide phase. Bartlett and James (1979) and Eary and Rai (1987), however, found that chromium also can be oxidized from Cr(III) to Cr(VI) in soils containing manganese oxide and thus be mobilized. Studies by Eary and Rai (1987) and Fendorf and Zasoski (1992) indicate chromium oxidation by δMnO_2 occurs readily below a pH of about 5.5, but is restricted by the precipitation of $Cr(OH)_3$ at higher pH values. These studies also indicate that the presence of oxygen does not appear to directly influence the oxidation state of chromium under the pH conditions found in the natural environment.

The field of stability of $Cr(OH)_3$ is illustrated in the pe-pH diagram presented in Figure 1. This figure indicates that the mobility of chromium is limited under moderately reducing and neutral to alkaline pH conditions. The presence of ferrous iron tends to further increase the field of stability of chromium hydroxide due to the formation of mixed iron-chromium hydroxide solid phases (Eary and Rai 1988 and 1989; Sass and Rai 1987).

Adsorption is also an important mechanism influencing the migration of hexavalent chromium under oxidizing conditions (Adriano 1986, Rai et al. 1989, and Zachara et al. 1987 and 1988). Chromium (VI) is adsorbed under acidic to moderately alkaline conditions by mineral solids that have exposed inorganic hydroxyl groups on their surfaces. The degree of adsorption tends to increase with decreasing pH as a result of protonation of surface hydroxyl sites and the aqueous speciation of Cr(VI).

2.2 FATE AND TRANSPORT OF CHROMIUM IN SOILS AND GROUNDWATER SYSTEMS

The contamination of groundwater systems typically results from the release of hexavalent chromium to surface soils via facilities such as landfills or disposal pits. Thus, chemical processes acting on chromium in the unsaturated soil zone are of environmental importance. A review of the literature also indicates that chemical processes influencing chromium migration may significantly change once hexavalent chromium enters a groundwater system (WHC 1993a).

The chromium concentration of uncontaminated soils is largely determined by the parent material and is highest for soils derived from igneous rocks and from shale. Soils in the United States typically range from about 25 ppm (sandy sediments) to 100 ppm (clay-rich soils), with chromium tending to be associated with the finer grain-size fractions (Richard and Bourg 1991 and WHC 1993a). Chromium in soils occurs as chromite, iron-chromium oxyhydroxides, and as sorbed Cr(III) and Cr(VI) species.

Hexavalent chromium is often reduced to Cr(III) in the soil environment owing to the presence of reducing agents such as ferrous iron or organic

matter (James and Bartlett 1983) and is consequently immobilized. Reduction will not occur, of course, if these reducing agents are not present. Such may be the case for Hanford Site soils, which are typically low in organic matter. Trivalent chromium may even be oxidized to the hexavalent state if manganese oxides are present in a soil (Bartlett and James 1979 and Eary and Rai 1987). The determination of the amount of hexavalent chromium present in a soil is usually accomplished by extraction followed by a colorimetric measurement employing diphenylcarbazide. Bloomfield and Pruden (1980) warn, however, that the presence of organic matter may interfere with this approach and utilized instead an absorptiometric method for detemination of hexavalent chromium in soils.

Once hexavalent chromium has entered a groundwater system, it is typically behaves as a conservative chemical constituent unless it is reduced to trivalent chromium. That is, Cr(VI) is typically not sorbed to a significant extent in neutral to alkaline solutions since it is an anionic species and thus will transported at approximately the same velocity as the average groundwater flow rate (Richard and Bourg 1991). This may be the case for portions of the Hanford Site unconfined aquifer that contain hexavalent chromium and appear to have an oxidized nature. Under some situations, however, adsorption of hexavalent chromium on aquifer solids may slow migration through an aerobic groundwater system. This is related to the presence of hydroxylated sites on oxide or clay surfaces (Zachara et al. 1987 and 1988), and tends to become more significant as pH decreases. Stollenwerk and Grove (1985), for example, observed significant adsorption of Cr(VI) to an alluvium associated with a contaminated aquifer. They observed that the zero point charge of the alluvium was approximately 8.3, and the alluvium had a positive net charge at the groundwater pH of 6.8. Iron oxide and hydroxide coatings on the alluvial particles were indicated to be responsible for the adsorption of Cr(VI).

It is likely that hexavalent chromium is reduced upon entering some groundwater systems and hence precipitated as iron-chromium oxyhydroxides. This situation may exist since air is not present in a saturated aquifer as a discrete gas phase. The solubility of oxygen in water is only about 7 ppm, so a groundwater system can readily become anaerobic if reducing agents are present (e.g., organic matter or ferrous iron-bearing minerals) and the groundwater residence time is sufficient. Thus Chrostowki et al. (1991) observed that hexavalent chromium is present in soils at a waste site in New Jersey, but absent in aquifer materials below the water table. They suggested that the groundwater is anoxic due to consumption of dissolved oxygen by ferrous iron, while the overlying soil is aerated. Thus, Cr(VI) is stable in the unsaturated soils but reduced by dissolved organic matter in the aquifer and subsequently precipitated.

There is evidence to indicate that hexavalent chromium occurs naturally in some soils and groundwater systems. As mentioned above, chromium in soils may be oxidized from the trivalent to hexavalent state if manganese oxides are present in a soil (Bartlett and James 1979 and Eary and Rai 1987). Chromate has also been reported to occur in nitrate deposits of the Atacoma Desert in South America (Beitel 1976 and Meller 1946). Instances of naturally occurring Cr(VI) in groundwater systems have also been described (Robertson 1975 and Ridley and Martinelli 1992).

2.3 FATE AND TRANSPORT OF CHROMIUM IN FLUVIAL AND ESTUARINE ENVIRONMENTS

The concentration of chromium in U.S. river waters ranges from less than 0.5 ppb to 100 ppb or greater (WHC 1993a, Richards and Bourg 1991, Cutshall 1967). In ocean water, the mean concentration is 0.3 ppb and ranges from 0.2 to 50 ppb. The exact form of chromium in surface waters is generally not well defined, but most of the soluble chromium is probably present as Cr(VI). Cr(VI) remains in solution until reduced to Cr(III), generally as a result of reacting with organic matter (NRCC 1976). A small amount of Cr(III) may be transported in solution as hydroxo or organic complexes (EPA 1984).

Chromium contamination in river systems commonly is a result of contribution from point sources, such as discharges from storm sewers or wastewater effluent outfalls, or distributed sources, including recharge from rainwater runoff over contaminated land surfaces or from contaminated aquifers.

Studies cited in WHC (1993a) indicate that chromium is transported in rivers as dissolved hexavalent chromium or suspended particles containing chromium. Hexavalent chromium may be reduced to trivalent chromium if sufficient organic matter is present and precipitated as chromium hydroxide. This is possible, for example, if disposal of municipal wastes to a river lead to anaerobic conditions. Under normal aerobic conditions, however, the hexavalent chromium may be transported a significant distance downstream as dissolved species and adsorbed to suspended particles.

There is a tendency for the suspended particulate matter in rivers to be deposited upon reaching estuarine or prodelta areas. This is due mainly to flocculation of iron-organic matter colloids that occurs as a result of increasing salinity (Sholkovitz et al. 1978). This is consistent with the observation that chromium content tends to be highest in the smaller grain size fractions in estuarine environments and is typically associated with high organic and iron content (U.S. Department of the Interior 1986). The estuarine environment is thus susceptible to contamination by chromium, as well as other heavy metals. Cranston and Murray (1980), for example, have noted that some of the dissolved chromium in the Columbia River is removed by flocculation and sorption upon reaching the estuary.

There is also a tendency for chromium and other heavy metals to accumulate in estuarine regions that are anaerobic in character, as indicated by the presence of hydrogen sulfide (Smillie et al. 1981) and organic matter. Concentrations in European estuaries have been observed to range from 3.9 ppm in intertidal sands to 162 ppm in anaerobic muds.

3.0 CHROMIUM DISTRIBUTION IN GROUNDWATER OF THE 100-D AND 100-H AREAS

An understanding of the distribution of chromium in the unconfined aquifer of the 100-D and 100-H Areas is necessary for identifying the major sources of contamination and migrational pathways. This is especially important since knowledge of the conditions under which contamination occurred, the location and timing of the discharges, and the concentration and exact form of the chromium waste is limited. This section describes the current distribution of chromium contamination in the groundwater and summarizes what is known about past practices responsible for this contamination.

Figure 2 illustrates the distribution of total dissolved chromium in the Hanford Unconfined Aquifer of the 100-D and 100-H Areas in October of 1992 as interpreted from data present in the Hanford Environmental Information System (HEIS). Chromium concentrations are typically highest for groundwater samples collected in the 100-D Area, but elevated levels are also associated with the groundwater of the 100-H Area. Note that the total area of the aquifer containing greater than 50 ppb chromium (the Model Toxics Control Act Cleanup Level) is several square miles in extent.

The distribution of chromium contamination in 100-D groundwater in October of 1992 is shown in greater detail in Figure 3. Chromium levels are typically similar in filtered and unfiltered samples from the 100-D Area, indicating that the bulk of the chromium is in solution and thus mobile (Dresel et al. 1993). The highest groundwater chromium concentrations in the 100-D Area are in the vicinity of well D5-15, which commonly exceeds 1500 ppb chromium. This well is located just north of the 100-D reactor. Sodium dichromate ($Na_2Cr_2O_7$) was used as a corrosion inhibitor in the single-pass cooling reactors at the Hanford Site, and chromic acid was employed in decontamination activities. Thus, the probable source of most chromate groundwater contamination in the 100-D Area can be attributed to the disposal of chromium-containing wastes and cooling water in the trenches and basins associated with the reactor. Note also that a region of lower chromium concentrations in Figure 3 located along the Columbia River about a half kilometer northwest of the D reactor. This arises from dilution associated with effluent from the 100-D Ponds (Hartman 1994).

Chromium has also been detected at elevated levels in groundwater over a large portion of the 100-H Area (Figures 2 and 4). Although some of the contamination in this area may be due to transport from 100-D, there are potential chromium sources in the 100-H Area. Possible chromium sources in the 100-H Area include disposal of sodium dichromate near the reactor building and to the 107-H Liquid Waste Trench, and chromium in acid wastes stored in the 183-H Solar Evaporation Basins (Peterson and Connelly 1992). Dresel et al. (1993) reported that the highest concentration of chromium measured in the 100-H Area during 1992 was from well 199-H4-14, located between the H Reactor Building and the 183-H Solar Evaporation Basins, with a maximum level of 410 ppb in the July 1992 sample. Figure 4 indicates that chromium is lower in concentration downgradient of the 183-H Solar Basis, suggesting that dilution by effluent may be occurring.

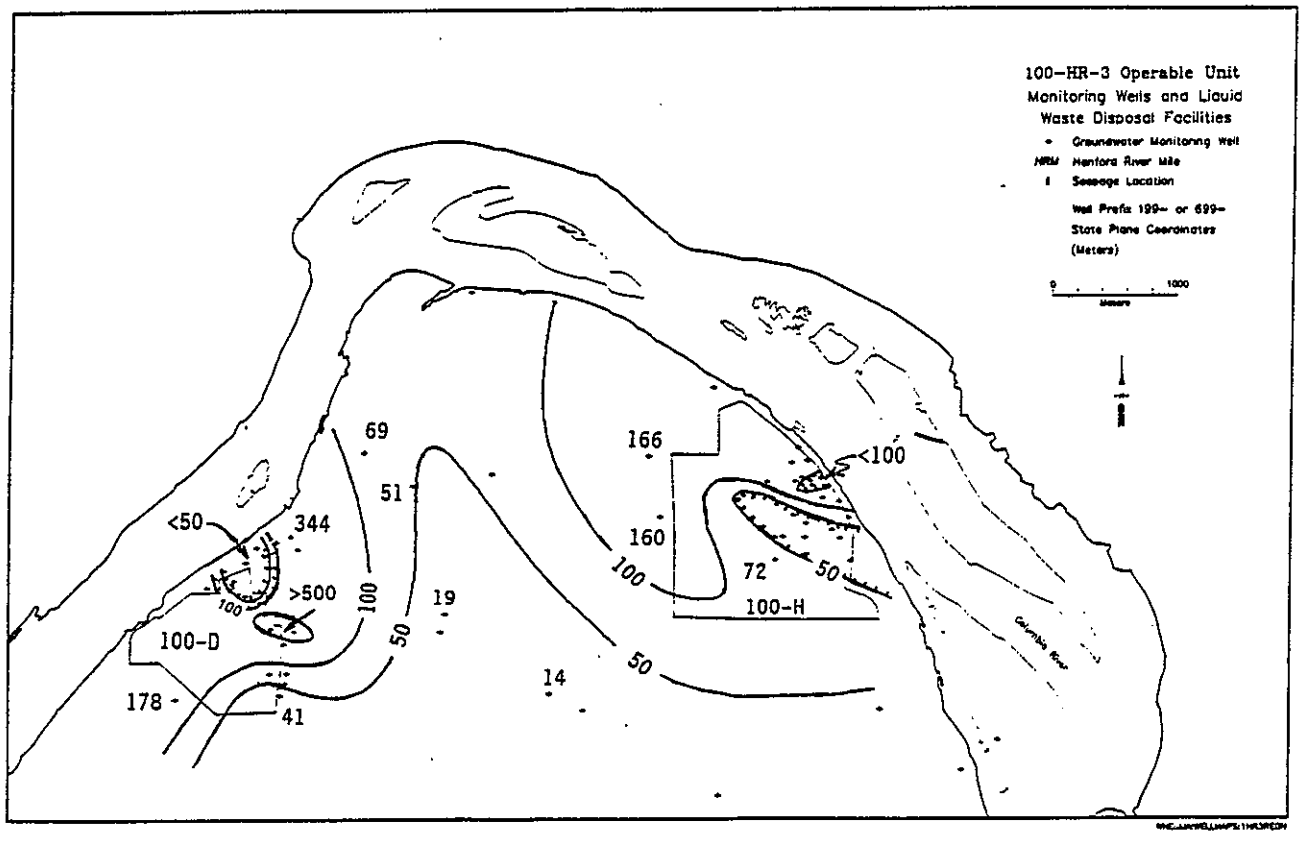

Figure 2. Chromium Distribution in the Hanford Site Unconfined Aquifer of the 100-D and 100-H Areas. Data shown is total chromium concentration values in ppb for filtered groundwater samples collected in October of 1992.

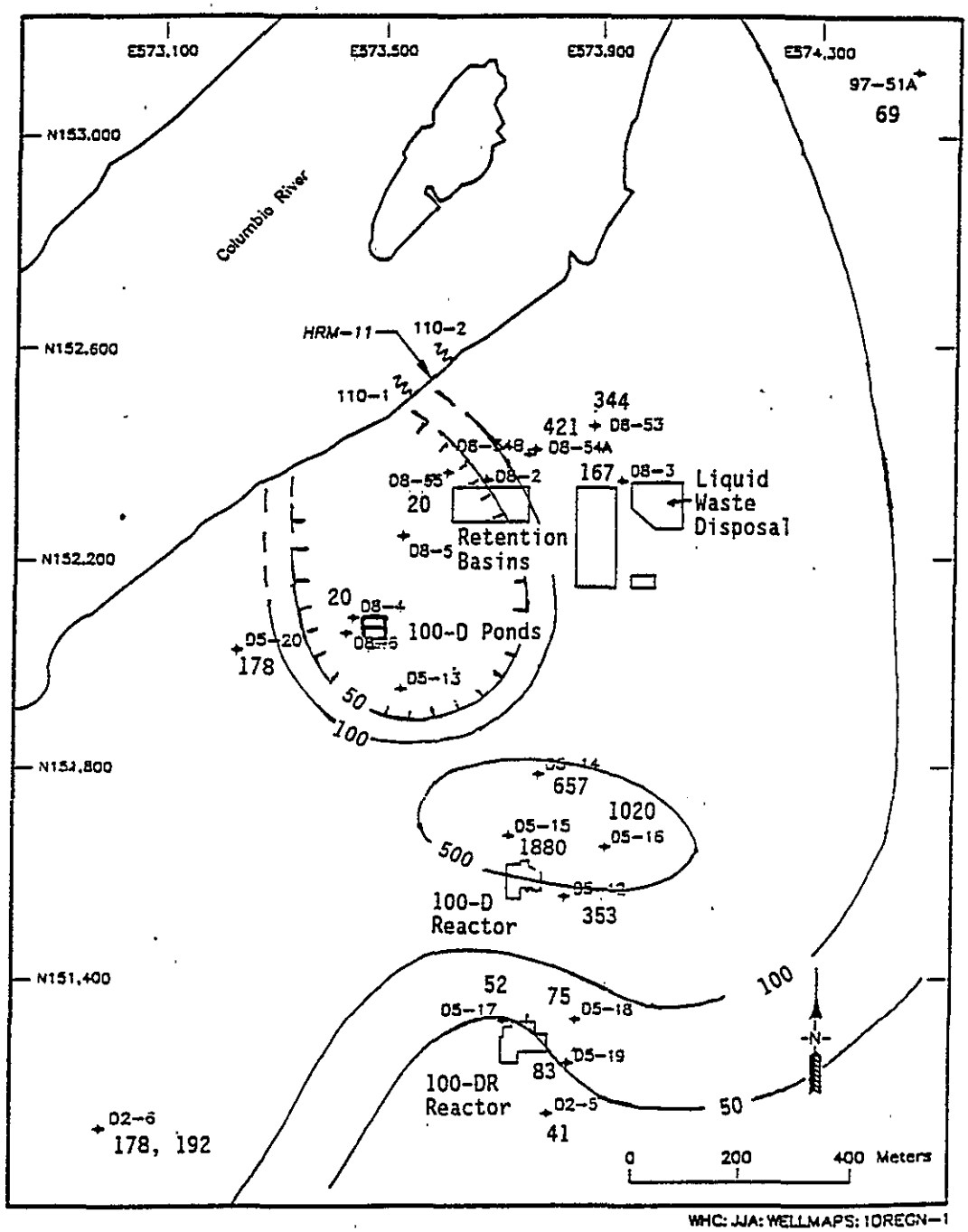

Figure 3. Chromium Distribution in the 100-D Area. Data shown is total chromium concentration values in ppb for filtered groundwater samples collected in October of 1992.

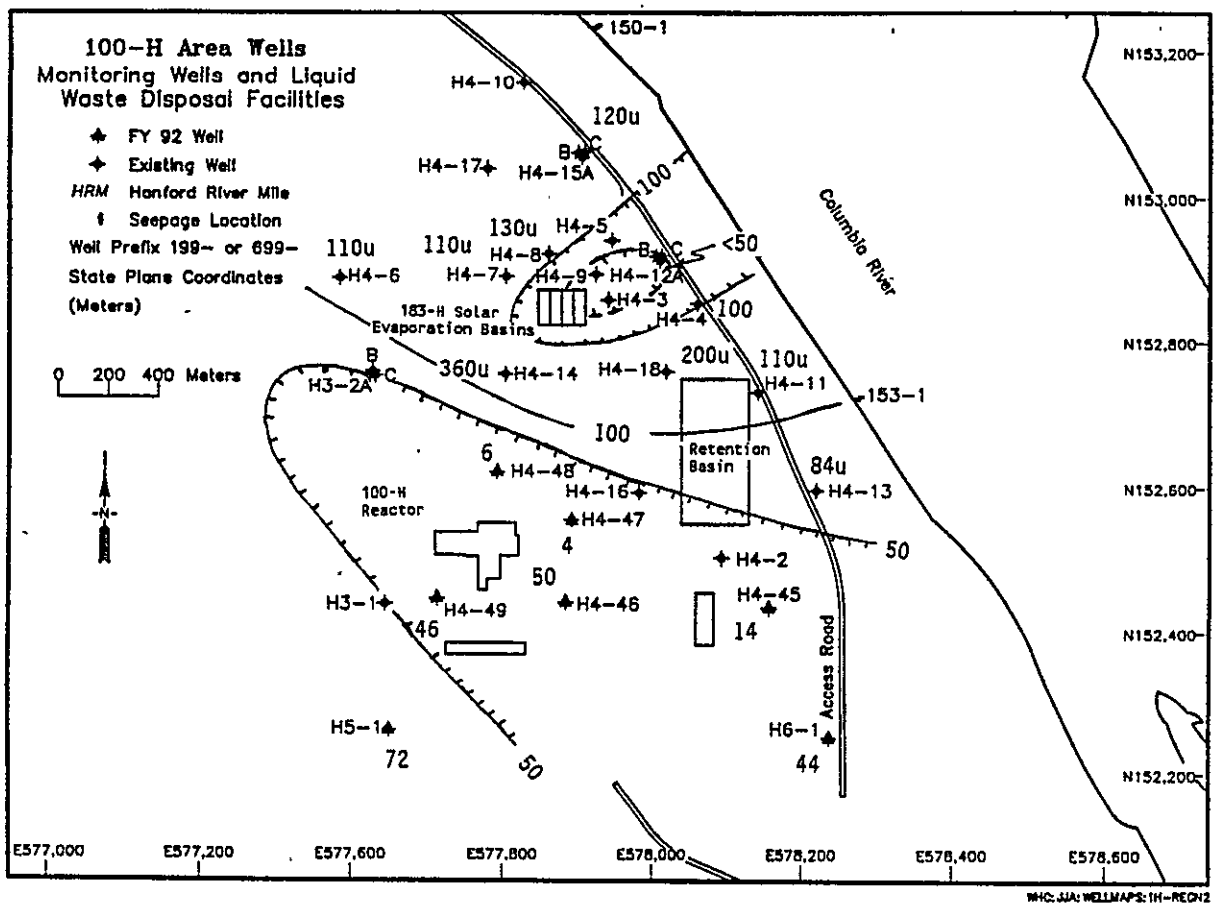

Figure 4. Chromium Distribution in the 100-H Area. Data shown is total chromium concentration values in ppb for filtered groundwater samples collected in September through November of 1992, and unfiltered samples (indicated by u suffix) collected in October of 1992.

4.0 CHROMIUM SPECIATION DETERMINATION OF WATER SAMPLES

4.1 METHODS

Sampling and analysis methods used in this project are those specified in WHC (1988 and 1993b). DOE-RL (1992a) also provides guidelines relevant to collecting seep and river water samples along the Hanford Reach.

4.1.1 Sample Collection

Groundwater samples were collected per EII 5.8 "Groundwater Sampling" (WHC 1988). Collection of water from seeps and driven well points were accomplished using a peristaltic pump. River water samples were collected adjacent to the 100-D and 100-H Areas as indicated in WHC (1993b). A composited sample of river water was also collected for use in the mixing study (Section 6). In addition, a sample of Columbia River water (designated "upriver sample") was collected several miles below Priest Rapids Dam.

Collection of water samples for offsite analysis included separate aliquots for acidified unfiltered metals, acidified filtered metals, pH, anions, nitrite-nitrate, conductivity, total organic carbon (TOC), total inorganic carbon (TIC), and hexavalent chromium. Additional portions were collected for field and onsite determination of hexavalent and total chromium and other constituents. In general, one blank and one duplicate sample were collected for each sample type (i.e., groundwater, seep water, and river water). Shipping of samples to offsite laboratories was performed as described in EII 5.11 "Sample Packaging and Shipping" and included maintenance of chain of custody documentation as required by EII 5.1 "Chain of Custody" (WHC 1988).

4.1.2 Sample Analysis

Analyses conducted by offsite laboratories included analysis of cations and metals by inductively coupled plasma emission spectrometry (ICP) per CLP contract, anions by ion chromatography (IC) per EPA method 300.0, pH by SW-846 method 9040, nitrite-nitrate by EPA method 353.1, conductivity by EPA method 120.1, TOC by SW-846 method 9060, and TIC by SW-846 method 5310B. In addition, hexavalent chromium was analyzed by an offsite laboratory using the diphenylcarbazide spectrophotometric method per EPA SW-846 method 7196.

The data associated with offsite laboratory analyses of water samples are presented in Appendix A. Also indicated are WHC sample numbers, site identification, date, time, and sample type. Laboratory-assigned data qualifiers (Q flags) are also presented, where U indicates that an analyte was not detected (less than or equal to the quantitation limit) and B indicates that the analyte was also found in an associated blank.

All samples were shipped as quickly as possible to offsite laboratories. It generally requires several days, however, from the time of sample collection until they are received by the laboratories. Holding time limits were not exceeded for most of the analytes. Hexavalent chromium has a holding time of only 24 hours, however, and thus holding time was exceeded since shipping time requires more than 24 hours. This does not invalidate positive

detection values, but renders non-detects unusable from a regulatory standpoint.

This study also included field and onsite laboratory determinations of hexavalent chromium. This was undertaken primarily to satisfy the 24 hour holding time limitation associated with hexavalent chromium and also to test the validity of the field method. Hexavalent chromium was analyzed per WHC method LA-265-401, which is equivalent to the SW-846 7196 diphenylcarbazide method. In addition, total chromium was analyzed onsite per WHC method LA-265-402, alkaline hypobromite oxidation. These two methods employ a spectrophotometer and are conducted with prepared reagent powder pillows supplied by the Hach Company. Quality control samples were also analyzed per WHC procedures to ensure acceptable accuracy and precision. Blanks were prepared using ASTM type II water in this task and all sampling and analytical work conducted during this study.

Chromium speciation of seep and river water samples was also performed by PNL using the method presented in Cranston and Murray (1978 and 1980). This approach provides detection limits in the nanomolar range for dissolved chromium, dissolved Cr(III), and particulate chromium. Dissolved Cr(VI) is then calculated by difference.

4.2 CHROMIUM SPECIATION OF GROUNDWATER SAMPLES

The hexavalent and total chromium analytical determinations associated with all groundwater samples collected during this study are presented in Table 1. The hexavalent chromium determinations performed by method 7196 must be considered as estimates, owing to the inability to ship samples to offsite laboratories within the specified holding time (24 hours). The results are consistent, however, with the onsite determinations (Cr(VI), Hach) that were performed within 24 hours. It is concluded that the Hach method (performed as specified by WHC LA-25-401) and method 7196 are both acceptable approaches for measurement of hexavalent chromium.

The results presented in Table 1 for total chromium by ICP and the Hach method (WHC LA-265-402) are also consistent for the groundwater samples collected. Note that in general total chromium values are somewhat higher for unfiltered than for filtered splits of each sample. This is attributed to the presence of particulate matter (sediment or corrosion products) associated with unfiltered samples.

The total chromium and hexavalent chromium values obtained for these samples are essentially equal, considering the uncertainty associated with the methods. It is concluded that the elevated total chromium concentrations associated with filtered samples collected in the 100-D and 100-H Areas represent dissolved hexavalent chromium. Unfiltered total chromium values may not be equivalent to hexavalent chromium, however, since chromium associated with particulate matter is generally in the reduced state (i.e., the trivalent oxidation state or metallic chromium).

Table 1. Hexavalent and Total Chromium Analytical Data in mg/L for Groundwater Samples Collected in the 100-D and 100-H Areas. WHC sample numbers are indicated by the B0 prefix.

Well #	Date Time	Cr(VI), 7196 unfiltered	Cr(VI), Hach	Cr_T, ICP	Cr_T, Hach
D5-15	7/13/93 08:47	--	1.26f	--	1.85uf 1.80f
H4-4	7/13/93 09:40	--	0.05f	0.075uf B08QZ0	0.05uf 0.05f
H4-3	7/13/93 10:15	--	0.13f	0.180uf B08QY9	0.18uf 0.16f
D5-15	5/13/94 09:20	1.65 BOBML3	1.1f 1.2f 1.45f	1.59uf BOBML1 1.40f BOBML2	1.45f
D5-15 (dup)	5/13/94 09:25	1.66 BOBML6	1.6f 1.3f	1.65uf BOBML4 1.50f BOBML5	1.3f
D5-16	5/13/94 11:15	--	0.78f 0.81f	--	0.80f
D8-53	5/13/94 12:00	0.41 BOBML9	0.32f 0.35f 0.34uf 0.38uf	0.329uf BOBML7 0.368f BOBML8	0.36f 0.35uf
H4-14	5/13/94 13:30	<0.05 BOBMM2	0.04f 0.04f	0.053uf BOBMM0 0.051f BOBMM1	0.03f
H4-11	5/13/94 14:22	<0.05 BOBMM5	0.06f 0.06f	0.064uf BOBMM3 0.066f BOBMM4	0.05f
H4-12C	5/13/94 15:00	--	0.26f 0.27f	--	0.24f
Equipment Blank	5/13/94 16:00	<0.05 BOBMM8	0.00f 0.00f	≤0.004uf BOBMM6 ≤0.004f BOBMM7	0.00f

f = filtered sample
uf = unfiltered sample
-- not analyzed
All samples analyzed by EPA SW-846 Method 7196 were unfiltered.

4.3 CHROMIUM SPECIATION OF SEEP AND WELL POINT WATER SAMPLES

Hexavalent and total chromium analytical data for the seep water samples collected are presented in Table 2. All Cr(VI) determinations by the 7196 method were non-detects (<0.05 mg/L). The Cr(VI) Hach method determinations were similar to the total chromium concentrations obtained by ICP for filtered samples, indicating that most of the dissolved chromium occurs in the hexavalent oxidation state in the seeps.

A driven well point was also utilized to obtain water samples from the sediment along the edge of the river in the 100-D Area. The drive point consisted of a length of steel screen tubing about three feet long with a solid steel point. The point was hammered to a depth of 7 to 12 inches at various locations along shore and about one or two feet inshore from the water line. A depth of 18 inches was required at Well Point #6, however, which was slightly further from the river. After insertion, water was allowed to flow into the drive point through the screen and then sampled by peristaltic pump through a clean length of plastic tubing placed within the drive point. Six of these samples were collected at separate well point locations on March 31, 1994, and one location (Well Point #5) was resampled on April 1, 1994 (Tables 2 and 3).

Most of the total chromium determinations for the driven well point water samples were performed on unfiltered samples using the Hach method. As indicated in Table 3, the unfiltered total chromium values were significantly higher than the unfiltered Cr(VI) values. The total chromium determinations of these samples are unlikely to represent true dissolved chromium concentrations owing to the presence of a significant amount of sediment present in the samples, which releases Cr(III) during the performance of the analysis. This is illustrated by comparison of the chromium determinations associated with a water sample collected at location Well Point #5 on April 1, 1994 (Table 2). Note that Cr(VI) and total chromium concentrations for the filtered portions were similar for this sample, although very low. The total chromium concentration, in constrast, was much higher than expected for dissolved chromium and clearly represents chromium associated with particulate matter in the sample.

The hexavalent chromium determinations presented in Table 3 are considered to be valid, however, since the Hach method for Cr(VI) does not utilize agents that will readily release or generate Cr(VI) from particulate matter. Table 3 also presents conductivity measurements reported for the well point samples. A direct correlation is observed between the Cr(VI) concentrations and conductivity of the samples, as illustrated in Figure 5. This suggests that the concentration of Cr(VI) in these samples is related to the degree of dilution associated with the mixing of groundwater and river water in the sampling area. This is further illustrated in Figure 5 where it is shown that the well point samples lie along a mixing line between a river water endmember and a groundwater endmember, represented by well D8-53.

Table 2. Hexavalent and Total Chromium Analytical Data (mg/L) for Seep Water Samples Collected in the 100-D and 100-H Areas.

Location	Date Time	Cr(VI), 7196 unfiltered	Cr(VI), Hach	Cr_T, ICP
Seep 153-1	3/17/93 08:30	--	0.03uf 0.05uf	0.045uf B08BD1 0.050f B08BD2
Seep 110-1	3/26/93 10:00	--	0.14uf	0.276uf B08BD7 0.247f B08BD8
Seep 110-1	3/31/94 09:15	<0.05 B0BMJ8	0.03uf	0.026uf B0BMJ6 0.025f B0BMJ7
Seep 110-1	4/1/94 08:00	<0.05 B0BMK1	0.01uf	0.025uf B0BMJ9 0.016f B0BMK0
Well Pt #5	4/1/94 09:00	<0.05 B0BMK4	0.01f	12.7 uf B0BMK2 0.022f B0BMK3
Seep 110-1 (dup)	4/1/94 9:45	<0.05 B0BMK7	0.02f 0.02uf	0.020uf B0BMK5 0.021f B0BMK6
Equipment Blank	4/1/94 11:30	<0.05 B0BML0	0.00f	≤0.003uf B0BMK8 ≤0.004f B0BMK9

Table 3. Hexavalent and Total Chromium Analytical Data (mg/L) and Conductivity (μs/cm) of Driven Well Point Water Samples Collected at 100-D.

Location	Date Time	Cr(VI), WHC 7196	Cr_T, Hach	Cond, μs/cm
Well Pt #1	3/31/94 10:15	0.08uf 0.09uf	0.12uf 0.13uf	183 188
Well Pt #2	3/31/94 10:30	0.06uf 0.06uf	0.14uf 0.14uf	187 188
Well Pt #3	3/31/94 10:35	0.04uf 0.04uf	0.12uf 0.14uf	177 176
Well Pt #4	3/31/94 10:40	0.00uf 0.00uf	0.10uf 0.09uf	145 144
Well Pt #5	3/31/94 11:00	0.02uf 0.03uf	0.10uf 0.10uf	155 157
Well Pt #6	3/31/94 11:10	0.10uf 0.10uf	0.18uf 0.18uf	193 193

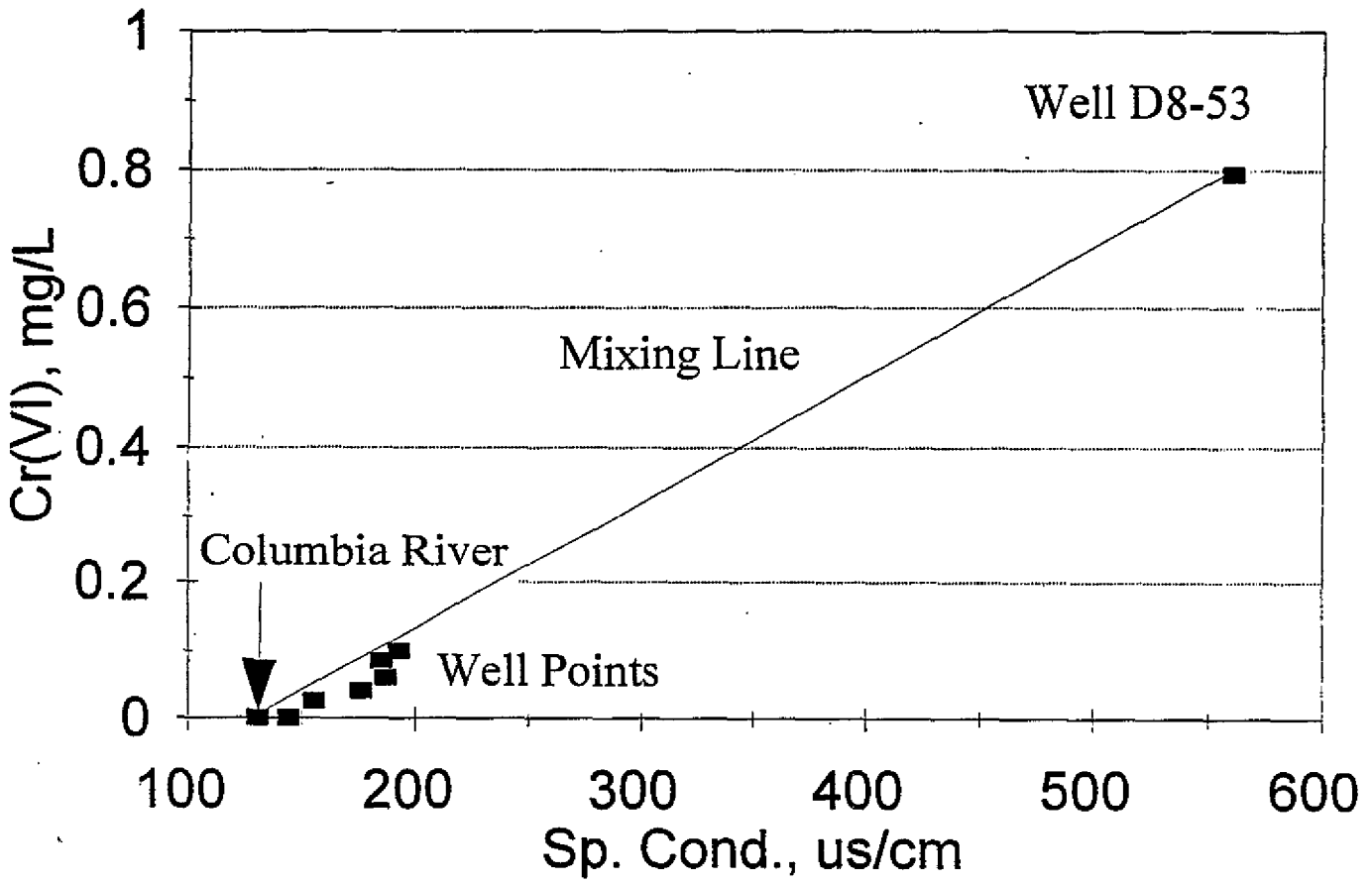

Figure 5. Cr(VI) Concentrations versus Specific Conductivity for Well Point Water Samples.

A limited number of determinations of chromium speciation was also performed utilizing the method developed by Cranston and Murray (1978 and 1980). This included four replicate determinations of seep 153-1 below the retention basin in the 100-H Area (100-HS spring of Table 4). The average of these determinations indicates concentrations of 35.3 ppb of aqueous Cr(VI) and 2.1 ppb aqueous Cr(III) (i.e., 4.5 ppb sediment chromium plus aqueous Cr(III) - 2.4 ppb sediment chromium). This corresponds to a distribution of dissolved chromium of 94% Cr(VI) and 6% Cr(III). Table 2 presents an independent determination of chromium speciation for seep 153-1, where 47.5 ppb total dissolved chromium and 40 ppb Cr(VI) were measured by ICP and the Hach method, respectively. This corresponds to about 84% Cr(VI) and 16% Cr(III).

A sample collected from a spring upstream from seep 153-1 was also analyzed by the Cranston and Murray method and yielded similar results (sample 100-HN1 of Table 4). A set of replicates from seep 110-1 of the 100-D Area did not yield statistically meaningful results, however, apparently owing to the presence of excess sediment in the samples.

4.4 CHROMIUM SPECIATION OF COLUMBIA RIVER WATER SAMPLES

Hexavalent and total chromium analytical data obtained for Columbia River water samples by the 7196, Hach, and ICP methods are presented in Table 5. These are all essentially non-detect values.

Chromium speciation determinations of river water samples were also undertaken using the method of Cranston and Murray (1978 and 1980). Results for Columbia River Water samples collected at 100-H and 100-D on March 17 and 26, 1993, respectively, are presented in Table 4. A total dissolved chromium value of 0.55 ppb was obtained for the sample collected at 100-H, of which 0.45 ppb (82%) was Cr(VI) and 0.1 ppb (18%) was Cr(III). The results for the sample collected at 100-D indicate that Cr(III) was about 0.3 ppb and Cr(VI) was $\leq$0.2 ppb.

Analysis of Columbia River samples by the method of Cranston and Murray thus indicates that the maximum total chromium concentration along the 100 Area is about 0.5 ppb. Data associated with the sample from the 100-H Area indicates that most of this (about 0.45 ppb) is hexavalent chromium. Cranston and Murray (1980) reported total chromium concentrations of about 0.2 ppb in the lower end of the Columbia River, with an average of 62% as dissolved Cr(VI), 36% as particulate chromium, and <2% as dissolved Cr(III). Thus, it appears that sufficient chromium enters the river adjacent to the Hanford Site to produce slightly elevated concentrations relative to other portions of the river, but well below what is normally considered to be of concern.

Table 4. Cr-Speciation Determinations of Spring and River Water Samples Collected in March of 1993 Using the Cranston and Murray Method.

		Cr Fraction			
Sample	Source	Sediment Cr	Sediment Cr +Cr(III)(aq.)	Total Cr	Cr(VI)(aq.)
		ng ml^{-1}			
100-HS1	Spring	2.4	4.5	42.	37.
100-HS2	Spring	1.6	3.0	37.	34.
100-HS4	Spring	2.5	5.0	39.	34.
100-HS6	Spring	3.0	5.5	41.	36.
Mean 100-HS	Spring	2.4	4.5	39.8	35.3
S.D.		0.6	1.1	2.	2.
100-HN1	Spring	3.1	2.3	34.	31.
100-D2*	Spring	255.	202.	363.	108.
100-D4	Spring	39.	21.	242.	203.
100-D5*	Spring	832.	758.	900.	68.
Mean 100-D	Spring	375.	327.	502.	126.
S.D.		410.	384.	350.	69.
100-H3	River	1.0	1.1	1.5	0.4
100-H5	River	1.1	1.2	1.7	0.5
Mean 100-H	River	1.05	1.15	1.6	0.45
S.D.		0.1	0.1	0.1	0.1
100-D1	River	0.9	1.3	1.0	---
100-D3	River	0.9	1.0	1.2	0.2
Mean 100-D	River	0.9	1.15	1.1	---
S.D.		0.0	0.2	0.1	---

*high sediment contents.

Table 5. Hexavalent and Total Chromium Analytical Data (mg/L) for Columbia River Water Samples.

Location	Date Time	Cr(VI), 7196 unfiltered	Cr(VI), Hach	Cr_T, ICP
100-H	3/17/93 10:25	--	0.01uf	≤0.004uf B08BD3 ≤0.003f B08BD4
100-D	3/26/93 09:00	--	0.01uf	≤0.003uf B08BD5 ≤0.006f B08BD6
DI H_2O	3/26/94 09:00	--	0.00uf	--
Upriver	5/16/94 13:15	<0.05 BOBXG3	0.01f	≤0.004uf BOBXG1 ≤0.004f BOBXG2
Composite	5/16/94 15:00	<0.05 BOBMN1	0.00f	≤0.004uf BOBMM9 ≤0.004f BOBMN0
Equipment Blank	5/16/94 15:30	<0.05 BOBXG0	0.00f	≤0.004uf BOBMN5 ≤0.004f BOBXF9

5.0 CHARACTERIZATION OF RIVERBANK SEDIMENT SAMPLES

Four sediment samples were collected in the vicinity of seep 110-1 of the 100-D Area. These samples were characterized by a variety of methods, as described below. The primary objective of these studies was to obtain information regarding potential interaction between riverbank sediments and groundwater in the river/aquifer interfacial zone. An understanding of these processes is necessary for predicting the fate of Cr(VI) transported into this region and assessing the potential for uptake by sediments.

5.1 METHODS

The following methods or tests were employed to characterize the sediments associated with this study:

Bulk Mineralogy: See Appendix B

Clay Mineralogy: See Appendix B

Particle Size Distribution: See Appendix B

Major Elements of Sediments: PIXE spectroscopy

Total C: Coulometric method of Huffman (1977)

Crystalline Fe and Cr Oxides: Dithionite-citrate-bicarbonate method described by Olson and Ellis (1982)

Mn Oxides: NH_2OH method of Chao (1972)

Chromium extraction with water, 0.01 M Na_2HPO_4, 6M HCl

Sequential extraction of chromium - exchangeable, bound to carbonate, associated with amorphous iron oxides, associated with crystalline iron and manganese oxides, bound to organic matter, residual

Chromium Oxidation Quick Test: $CrCl_3$ method for determination of potential for oxidation of Cr(III) to Cr(VI) by soils as described in Bartlett and James (1979)

Batch sorption/reduction of Cr(VI) by sediment

5.2 RESULTS

Mineralogical composition and the particle size distribution of the four sediment samples collected for this study are presented in Tables 6 and 7. The samples are texturally sands with minor amounts of clay and silt, and are composed primarily of quartz and feldspar. The clay-sized fraction is predominantly smectite. Significant amounts of kaolin/serpentine are associated with the sand, silt, and clay fractions. Mica is a minor component of the sand and silt fractions.

Table 6. Mineralogical/Textural Analyses of Riverbank Sediment Samples by X-ray Diffraction.

Mineral	Sample Identification #1	#2	#3	#4
	wt %			
SAND FRACTION	83	73	71	78
Quartz	48	40	50	49
Feldspar	32	43	30	31
Hornblende	2	1	1	2
Mica	8	10	9	11
Kaolin/Serpentine	10	6	10	7
	wt %			
SILT FRACTION	13	10	10	13
Quartz	34	31	36	33
Feldspar	34	37	27	30
Hornblende	2	3	2	--*
Mica	9	12	11	14
Kaolin/Serpentine	21	12	11	12
Vermiculite/Chlorite	--	6	13	10
	wt %			
CLAY FRACTION	5	17	19	9
Illite	6	8	8	4
Kaolinite	4	3	6	3
Chlorite	2	2	2	1
Quartz	18	18	17	9
Feldspar	20	21	26	14
Vermiculite	5	5	4	3
Smectite	45	43	38	67
Layer Silicates Only	wt %			
Illite	10	13	14	6
Kaolinite	7	5	10	4
Chlorite	3	3	3	1
Vermiculite	9	9	6	4
Smectite	71	71	68	86

* -- = none detected

Table 7. Summary of Mineralogical Analyses of Riverbank Samples by X-ray Diffraction.

Mineral	Sample Identification			
	#1	#2	#3	#4
	wt %			
Quartz	45	35	42	43
Feldspar	32	39	29	29
Hornblende	2	1	1	1
Mica/Illite	8	10	9	11
Kaolin/Serpentine	11	6	9	7
Vermiculite/Chlorite	<1	2	2	2
Smectite	2	7	7	6

* -- = none detected

Semi-quantitative chemical analyses of the sediments were also performed by PIXE spectroscopy (Table 8). This data indicates that a significant amount of iron, manganese, and chromium is associated with the sediments and suggests that a significant metal oxide fraction may be present. Sediment #4 has the highest concentration of iron and is significantly enriched in chromium with an estimated concentration of 145 ppm.

A series of extraction and dissolution tests were also conducted on the four sediment samples (Tables 9, 10, and 11). The primary objective of this work was to determine the manner in which chromium is chemically situated within the soil solids. Table 9 presents the results of extraction tests performed to determine concentrations of Fe, Mn, Al, Si, and Cr associated with the crystalline iron oxide and the manganese oxide fractions of the riverbank sediments and for a soil collected within the 100-D Area. This information indicates that Sediment #4 is enriched in chromium within these fractions relative to the other riverbank sediments and contains much more chromium in the oxide fraction than does the soil sample collected at 100-D. Additional tests also indicated that the chromium associated with the riverbank sediments is not leachable with water or 0.01 M Na_2HPO_4, and is not in an exchangeable position or bound in an organic fraction (Table 11). It is concluded that the excess chromium associated with the riverbank sediments is situated in the oxide fraction, particularly in Sample #4 (Tables 9 and 11), and in a residual fraction. The latter is composed predominantly of the silicate minerals.

Peterson and Johnson (1992) collected sediment samples from seepage areas along the Hanford Reach of the Columbia River in 1991. They also observed elevated levels of chromium in several sediments sampled near the 100-D and 100-H Areas relative to other seepage areas and background references.

Batch tests involving the riverbank sediments and chromium solutions were also conducted to obtain information relevant to the potential mass transfer of chromium from pore solutions to sediments in the aquifer/river interfacial zone. These tests involved mixing the sediments with solutions containing Cr(III) or Cr(VI). The results of these tests are presented in Table 12, which indicates the concentration of Cr(VI) present in the solutions as a function of time. The tests conducted with the Cr(III) solutions indicate that the potential exists for conversion of a portion of the Cr(III) in solution to Cr(VI). This may be due to the presence of a reactive Mn(IV) fraction in the soils that oxidizes a minor amount of Cr(III) in the test solution. This appears to be a temporary trend, however, as the concentration of Cr(VI) subsequently decreases. The second series of batch tests conducted with Cr(VI) solutions indicates that the sediments have a strong tendency for uptake of Cr(VI) from the solutions. It is suggested that the mechanism for uptake is a chemical sorption process, involving reduction of Cr(VI) to Cr(III) and subsequent sorption/precipitation of Cr(III) by the soil oxide fraction. The agent responsible for reduction of Cr(VI) is probably organic matter and labile ferrous iron present in the riverbank sediments.

Table 8. Semi-Quantitatative Elemental Analyses of Riverbank Sediments.

	Sediment			
	#1	#2	#3	#4
	---------- $\mu g\ g^{-1}$ ----------			
Na	18800	18700	18800	20200
Mg	9900	10800	9200	11100
Al	91900	92300	70400	77000
Si	292000	283000	307000	290000
P	3100	3500	3300	3500
S	1500	1700	1400	1400
Cl	2800	3500	1900	2000
K	14500	14400	17900	16100
Ca	18500	21500	19200	23600
Ti	3900	4700	4400	5500
V	<120	<130	<130	<140
Cr	85	95	85	145
Mn	630	875	570	765
Fe	32100	38400	34400	43100

Table 9. Selected Chemical Properties of Riverbank Sediments.

Property	Units	Sediment #1	#2	#3	#4	100-D
Total C	$\mu g\ g^{-1}$	6200	9700	1100	3200	16500
Associated with Crystalline Iron Oxides [0.08 M NaS_2O_4 + 0.75 M Na_3-citrate, 1:30 Solid:Solution, Overnight Extraction (Olsen and Ellis, 1982)]:						
Fe	$\mu g\ g^{-1}$	3800	5000	2700	4100	2900
Mn	$\mu g\ g^{-1}$	240	450	120	200	120
Al	$\mu g\ g^{-1}$	450	500	300	500	360
Si	$\mu g\ g^{-1}$	1000	1200	500	900	650
Cr	$\mu g\ g^{-1}$	30	30	30	90	<20
Associated with Manganese Oxides [0.1 M NH_2OH + 0.01 M HCl, 1:50 Solid:Solution, 30-Minute Extraction (Chao, 1972)]:						
Fe	$\mu g\ g^{-1}$	1600	2500	1800	1200	180
Mn	$\mu g\ g^{-1}$	300	500	200	140	90
Al	$\mu g\ g^{-1}$	1300	1900	1400	1100	340
Si	$\mu g\ g^{-1}$	1200	1700	1100	1000	380
Cr	$\mu g\ g^{-1}$	17	22	20	32	<20

Table 10. Acid Extraction of Chromium from Riverbank Sediments.[1]

Treatment	Extraction Number 1	2	3	Total
	---------- μg Cr g^{-1} ----------			
Sediment #1	12	28	---*	40
Sediment #2	20	15	---	35
Sediment #3	10	8	---	18
Sediment #4	30	17	12	59

* --- = below detection [i.e., <10 ng Cr g^{-1}].

[1]Chromium was extracted from the sediments by three successive overnight treatments with 6 M HCl solutions. No chromium was detectable in extracts with H_2O or 0.01 M Na_2HPO_4 (pH 7).

Table 11. Sequential Extraction of Chromium from Riverbank Sediments.[1]

Form of Cr	Sediment 1	2	3	4
	---------- μg Cr g^{-1} ----------			
Exchangeable	---*	---	---	---
Carbonates	---	---	---	---
Amorphous Oxides	---	---	---	240
Crystalline Oxides	---	---	---	---
Organic Matter	---	---	---	---
Residual	50	55	75	---
TOTAL	50	55	75	240

* --- = below detection [i.e., <50 μg Cr g^{-1}].

[1]Chromium was extracted from Hanford River Bank Sediments by six successive treatments designed to remove, in sequence, chromium that is 1) exchangeable, 2) bound to carbonates, 3) associated with amorphous iron oxides, 4) associated with crystalline iron and manganese oxides, 5) bound to organic matter, and 6) residual.

Table 12. Variation in Cr(VI) Solution Concentrations in Batch Tests of Sediments Equilibrated with Cr(III) and Cr(VI) Solutions.[1]

Treatment	Equilibration Time		
	7 d	20 d	34 d
	------ ng Cr(VI) g^{-1} ------		
2.16 mg Cr(III) g^{-1} added			
Sediment #1	1900	390	750
Sediment #2	760	---*	---
Sediment #3	3090	1600	1880
Sediment #4	2900	300	700
Blank**	---	100	160
900 ng Cr(VI) g^{-1} added			
Sediment #1	100	---	---
Sediment #2	120	---	---
Sediment #3	465	165	115
Sediment #4	300	---	---
Blank	795	575	560

* --- = below detection [i.e., <60 ng Cr(VI) g^{-1}].
**Results calculated assuming 10 g soil present for comparison purposes.
[1]Soluble Cr(VI) measured after equilibration of riverbank sediments with 0.01 N $CaCl_2$ solutions containing 2.16 mg Cr(III) g^{-1} sediment or 900 ng Cr(VI) g^{-1} sediment.

6.0 GROUNDWATER AND RIVER WATER MIXING STUDY

In this task, a series of tests was conducted in which groundwater contaminated with Cr(VI) was mixed with a representative sample of Columbia River water in varying ratios. Each mixture was sampled over a period of several weeks and analyzed for Cr(VI) and other parameters. The primary objective of the mixing study was to assess the changes in concentration and speciation of dissolved chromium in the river water following mixing and the subsequent partitioning into the suspended particulate fraction or removal by precipitation.

6.1 SAMPLE COLLECTION

A large composite sample of Columbia River water (~40 L) was prepared for this study by combining a series of near-shore river water samples collected at ten locations between the 100-D and 100-H Areas on May 16, 1994. Collection of these samples was conducted by the direct sampling method as described in DOE-RL (1992b). Two samples were collected at each location: a 2-L sample in about six inches of water and a 2-L sample taken further from shore in about three feet of water. The second sample was collected about six inches off bottom. Sampling locations are shown in Figure 6. Analytical data for the composite sample is presented in Appendix A and in Table 5.

A five liter sample of groundwater was also collected from well D5-15 for the laboratory mixing study. This sample was taken on May 13, 1994, at the time groundwater samples were collected for water analysis (Appendix A and Table 1). The Cr(VI) concentration of this sample was determined to be about 1600 ppb.

6.2 DESCRIPTION OF MIXING TESTS

Portions of the composite sample of Columbia River water were transferred to nine reservoirs for evaluation of mixing of groundwater with river water (2 L of river water per reservoir). Each of these reservoirs was stirred constantly at a low rate and maintained at river temperature (8°C) for the duration of the tests.

Aliquots of water was taken from each reservoir for determination of Cr(VI) concentration by the diphenylcarbazide method. These samples were collected at the beginning of each test (after initiation of mixing) and at 4 hours, 1 day, 3 days, 7 days, and 21 days. Other data was also collected prior to and during the mixing experiments that are related to primary variables controlling the speciation of chromium. These determinations included concentration of suspended particulates, pH, redox potential (Eh), temperature, and Cr(VI) concentration.

The first reservoir contained river water as a control (Test 1). Portions of groundwater containing chromium were added to each of the next five reservoirs. The ratio of river water to groundwater was 1, 10, 100, and 500 in four of these reservoirs (Tests 2, 3, 4, and 5, respectively). This range of ratios was chosen to represent the natural environment, where a ratio

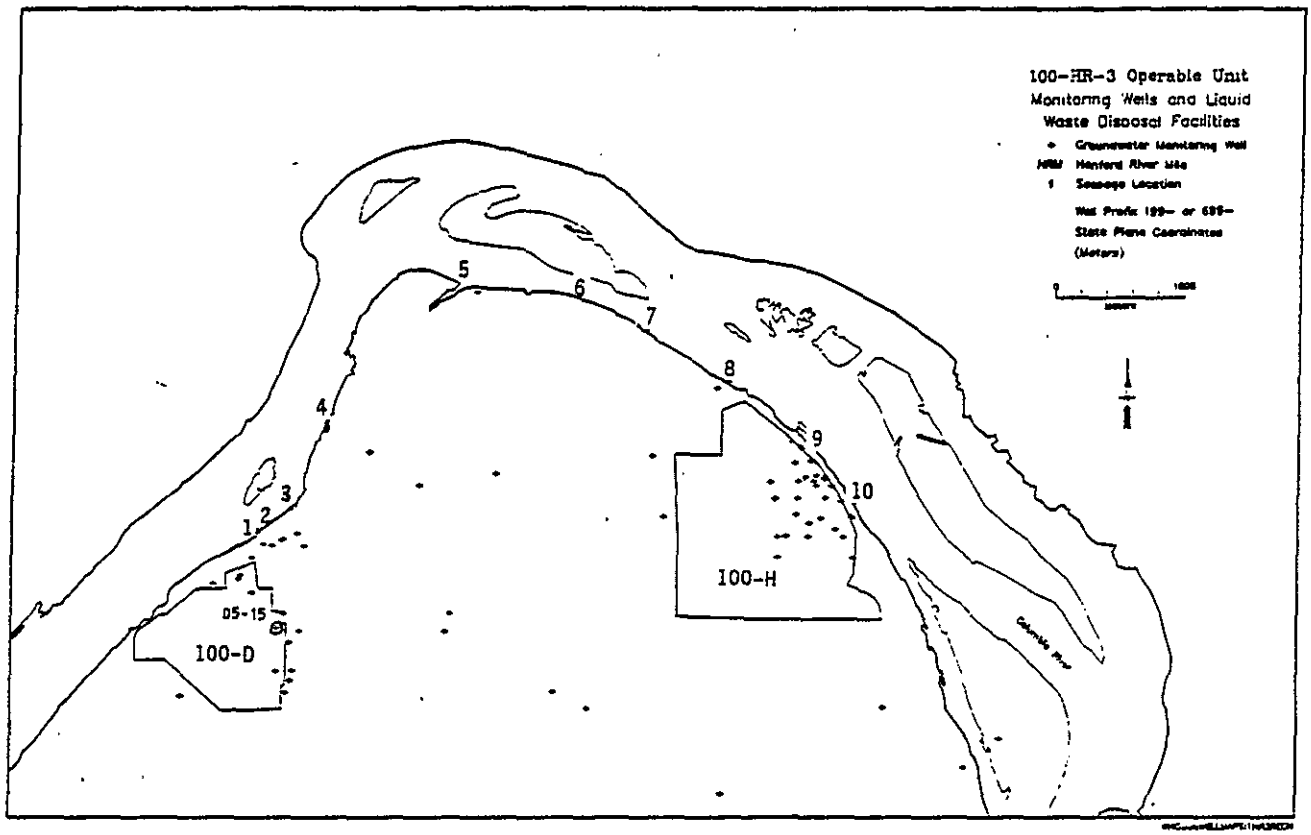

Figure 6. Locations of Riverwater Samples Collected for Columbia River Composite.

of 1 is analogous to mixing processes in the bed of the river while a ratio of 500 is representative of higher dilutions where river water greatly dominates the groundwater component. Information gained by comparing the data over this range should clarify the fate of chromium following its entry into the fluvial environment and provide a model for predicting spatial variations in the distribution and speciation of chromium.

A ratio of 10 was also used in the sixth reservoir (Test 6), but this reservoir was exposed to ultraviolet light during the test to evaluate photoreductive or photooxidative effects. A 2000 ppb Cr(VI) standard solution was added to the river water in the seventh reservoir (Test 7), also at a ratio of 10. The objective of this test was to provide a basis for determining if specific matrix effects associated with the groundwater sample materially affect the fate of chromium subsequent to mixing with river water.

The eighth 2-L volume reservoir contained only groundwater (Test 8). This reservoir served as a control to identify in changes in Cr(VI) concentration in the groundwater sample over the duration of the testing activities.

The last reservoir (Test 9) contained a mixture of filtered groundwater and river water. The ratio of river water to groundwater was 10 in this test. The objective of Test 9 was to evaluate the effect of suspended particulate matter on Cr(VI) concentration by comparison with the other tests.

6.3 RESULTS OF MIXING TESTS

The change in Cr(VI) concentration with time in the mixing tests is illustrated in Figure 7. The concentration of Cr(VI) did not change in Tests 2, 3, 6, 7, and 9, indicating no significant reduction of Cr(VI) occurred at river water to groundwater ratios of 1 or 10. Cr(VI) concentrations remained constant in the groundwater control test (Test 8) and no Cr(IV) was detected in the river water control (Test 1). A slight decrease in the concentration of Cr(VI) with time was reported for Tests 4 and 5, which were conducted at river to groundwater ratios of 100 and 500, respectively. These data are of semi-quantitative significance only, owing to the low concentrations of Cr(VI) involved, but suggest that some Cr(VI) may be reduced at high dilutions by organic or particulate matter associated with the river water.

Average values for pH and Eh during the tests were about 7.5 and 400 mvolts, respectively. A slight increase in both was observed during the tests. These changes were considered to be insignificant, however, and are probably related to aeration of the solutions during mixing. No well-defined trends were observed in suspended particulate concentrations during the tests, although Tests 4 and 5 exhibited a slight increase with time (Figure 8). An increase of suspended material in these two tests is consistent with the possible reduction and precipitation of Cr(VI) in the mixing tests conducted at high dilutions.

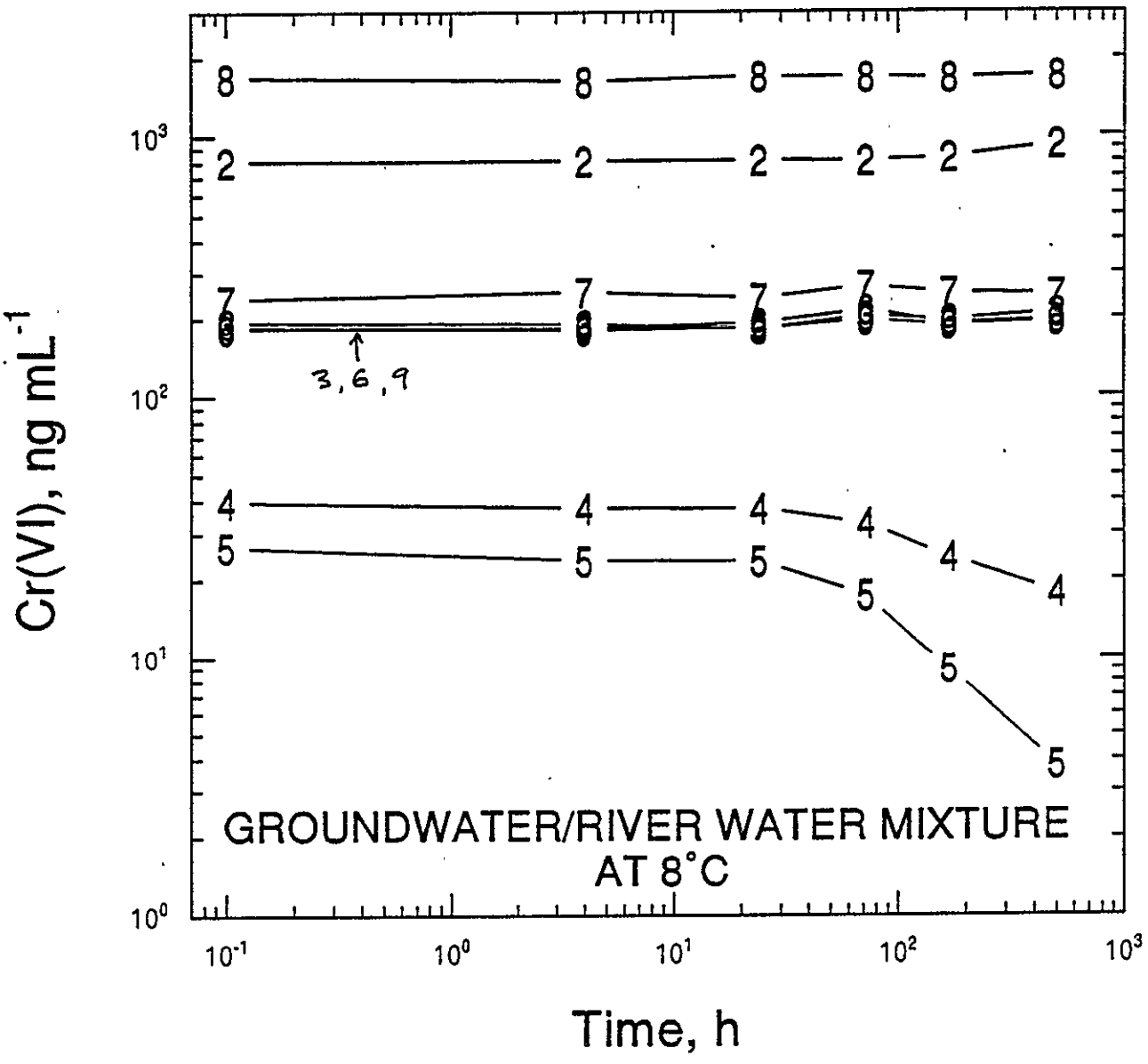

Figure 7. Cr(VI) Concentration versus Time for Mixing Tests.

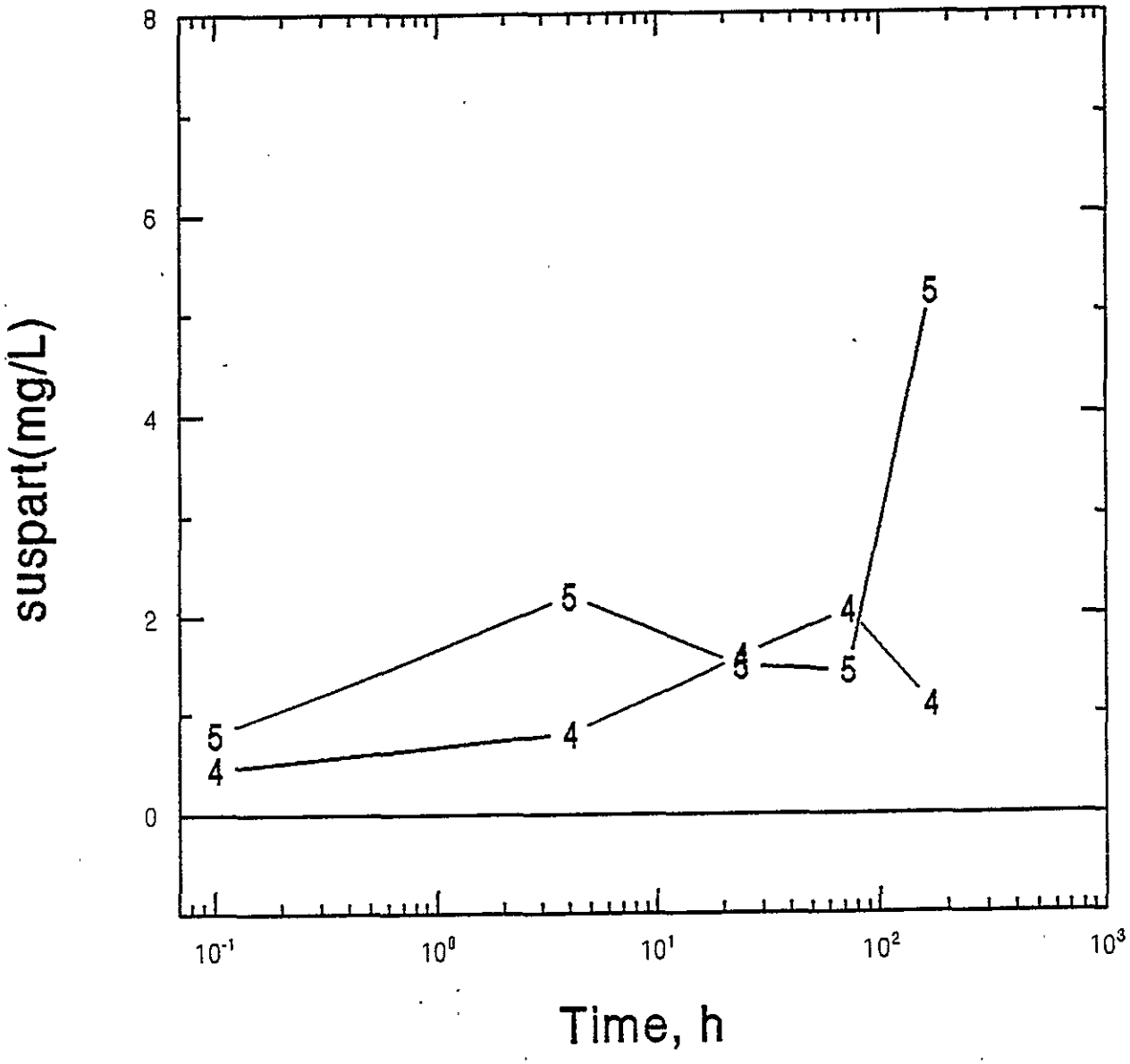

Figure 8. Suspended Particle Concentration versus Time for Tests 4 and 5.

7.0 CONCLUSIONS

Analysis of groundwater and seep water samples collected from the 100-D and 100-H Areas of the Hanford Site indicate that dissolved chromium occurs primarily in the hexavalent oxidation state. This is consistent with the known chemical characteristics of chromium. It is concluded that determination of Cr(VI) by the Hach method (spectrophotometric detemination using diphenylcarbazide) is a convenient and dependable approach, especially if appropriate quality control protocol are employed (i.e., adherence to WHC procedure LA-25-402 or EPA SW-846 method 7196). This method can be readily performed in the field, thus meeting the 24-hour holding time limitation associated with Cr(VI).

A field test was also performed in which pore water samples were recovered from riverbank sediments using a drive point. This approach proved to be an efficient method for sampling to depths as great as 18 inches. The recovered water samples were analyzed for Cr(VI) and conductivity immediately after sampling. A positive correlation between these parameters was identified, suggesting that a simple mixing model involving river water and groundwater explains the distribution of dissolved Cr(VI) concentrations in the aquifer/river transitional zone. It is recommended that this approach be utilized in future work to obtain flux estimates of Cr(VI) discharging from the 100 Areas into the Columbia River.

Sediment characterization activities were also conducted on riverbank sediments collected at 100-D. A positive enrichment of chromium was found in these sediments that appeared to be associated with the oxide fraction of the samples. Batch tests involving chromium solutions and the sediment samples suggest that Cr(VI) is transferred from riverbank pore solutions to the soil surfaces, probably through a reduction/sorption process. This process appears to be essentially irreversible, since the chromium is transferred to the sediment in the trivalent state as an insoluble oxide product.

The results of laboratory mixing tests suggest that Cr(VI) remains primarily in the hexavalent oxidation state after entering the Columbia River and mixing with river water, although a minor amount may be reduced and precipitated by interaction with suspended particulate matter. It is concluded that the dominant process associated with mixing, however, is a decrease in Cr(VI) concentrations owing to dilution. Thus, Cr(VI) behaves essentially as a conservative constituent during mixing. This is especially true if suspended particulate material is low and the solution is aerated (see also Cutshall 1967 and Cutshall et al. 1966). Analysis of Columbia River samples collected adjacent to the 100-D and 100-H Areas indicate that total chromium present in the river is 0.5 ppb or less. Data associated with a river water sample collected at 100-H indicates that most of the chromium present is in the hexavalent state.

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APPENDIX A

WATER CHEMISTRY ANALYTICAL DATA

Site Identification	153-1	Q	153-1	Q	100-H	Q	100-H	Q
Sample Type	seep		seep		river		river	
Date	3/17/93		3/17/93		3/17/93		3/17/93	
Time	8:30		8:30		10:25		10:25	
HEIS Sample No.	B08BD1		B08BD2		B08BD3		B08BD4	
Filtered/Unfiltered	unfilt.		filt.		unfilt.		filt.	
Quality Control Sample								
Aluminum (ug/l)	27.0	U	33.4	B	35.5	B	33.4	B
Antimony (ug/l)	18.4	U	18.4	U	18.4	U	18.4	U
Barium (ug/l)	27.3	B	28.1	B	28.0	B	28.3	B
Beryllium (ug/l)	0.50	U	0.50	U	0.50	U	0.50	U
Cadmium (ug/l)	1.6	U	1.6	U	1.6	U	1.6	U
Calcium (ug/l)	33400		36900		20800		21300	
Chromium (ug/l)	45.0		50.2		4.2	B	2.7	U
Cobalt (ug/l)	2.5	U	2.5	U	2.5	U	2.5	U
Copper (ug/l)	7.8	B	8.2	B	6.2	B	4.3	B
Iron (ug/l)	10.8	B	6.5	U	20.5	B	11.9	B
Magnesium (ug/l)	6880		7430		5140		5170	
Manganese (ug/l)	1.6	B	1.4	B	3.3	B	1.0	U
Nickel (ug/l)	3.0	U	3.0	U	3.0	U	3.0	U
Potassium (ug/l)	1280	B	1240	B	817	B	775	B
Silver (ug/l)	3.9	U	3.9	U	3.9	U	3.9	U
Sodium (ug/l)	4090	B	4330	B	2400	B	2410	B
Vanadium (ug/l)	2.5	U	2.5	U	2.8	B	2.5	U
Zinc (ug/l)	4.7	U	6.2	B	4.7	U	7.5	B
Chloride by IC (mg/l)	3.0				1.2			
Fluoride by IC (mg/l)	0.2				0.3			
Nitrite by IC (mg/l)	<0.1				<0.1			
Nitrate by IC (mg/l)	2.3				0.4			
Phosphate by IC (mg/l)	<0.4				<0.4			
Sulfate by IC (mg/l)	23				11			
Nitrite/Nitrate (mg-N/l)								
TOC (mg/l)								
pH								
Sp. Cond. (umhos/cm)								
TIC (mg/l)								

Site Identification	100-D	Q	100-D	Q	110-1	Q	110-1	Q
Sample Type	river		river		seep		seep	
Date	3/26/93		3/26/93		3/26/93		3/26/93	
Time	9:00		9:00		10:00		10:00	
HEIS Sample No.	B08BD5		B08BD6		B08BD7		B08BD8	
Filtered/Unfiltered	unfilt.		filt.		unfilt.		filt.	
Quality Control Sample								
Aluminum (ug/l)	45.2	B	24.6	B	9890		32.8	B
Antimony (ug/l)	18.6	U	17.9	U	18.6	U	17.9	U
Barium (ug/l)	30.4	B	29.7	B	166	B	66.8	B
Beryllium (ug/l)	0.30	U	0.50	U	0.35	B	0.50	U
Cadmium (ug/l)	1.4	U	1.7	U	1.4	U	1.7	U
Calcium (ug/l)	20600		21100		56200		54600	
Chromium (ug/l)	3.3	U	5.8	U	276		247	
Cobalt (ug/l)	2.9	U	3.8	U	6.2	B	3.8	U
Copper (ug/l)	9.1	B	4.2	U	25.9		4.2	U
Iron (ug/l)	46.4	B	17.7	B	10300		31.1	B
Magnesium (ug/l)	5120		5230		14000		11100	
Manganese (ug/l)	4.8	B	1.8	U	489		1.8	U
Nickel (ug/l)	4.2	U	6.1	U	12.9	B	6.1	U
Potassium (ug/l)	806	B	819	B	3710	B	2150	B
Silver (ug/l)	3.3	U	3.8	U	3.3	U	3.8	U
Sodium (ug/l)	2570	B	2430	B	8850		8040	
Vanadium (ug/l)	2.2	B	3.3	U	20.7	B	6.0	B
Zinc (ug/l)	12.6	B	12.4	B	239		9.0	B
Chloride by IC (mg/l)	1.3				19.2			
Fluoride by IC (mg/l)	0.2				0.3			
Nitrite by IC (mg/l)	<0.1				0.1			
Nitrate by IC (mg/l)	0.4				6.8			
Phosphate by IC (mg/l)	<0.4				<0.4			
Sulfate by IC (mg/l)	11				71			
Nitrite/Nitrate (mg-N/l)								
TOC (mg/l)								
pH								
Sp. Cond. (umhos/cm)								
TIC (mg/l)								

Site Identification	110-1	Q	110-1	Q	Well Pt.#5	Q	Well Pt.#5	Q
Sample Type	seep		seep		drive point		drive point	
Date	3/31/94		3/31/94		4/1/94		4/1/94	
Time	9:15		9:15		9:00		9:00	
HEIS Sample No.	B0BMJ6		B0BMJ7		B0BMK2		B0BMK3	
Filtered/Unfiltered	unfilt.		filt.		unfilt.		filt.	
Quality Control Sample								
Aluminum (ug/l)	39.00	B	26.20	B	1010000		105.00	B
Antimony (ug/l)	25.40	U	25.40	U	102		27.20	B
Barium (ug/l)	30.50	B	24.10	B	11200		29.90	B
Beryllium (ug/l)	0.30	U	0.30	U	47.6		0.40	B
Cadmium (ug/l)	2.60	U	2.60	U	74.2		2.60	U
Calcium (ug/l)	24500.00		20500.00		369000		22700.00	
Chromium (ug/l)	26.40		24.80		12700		21.70	
Cobalt (ug/l)	3.90	U	3.90	U	864		3.90	U
Copper (ug/l)	12.10	B	6.20	B	2210		7.00	B
Iron (ug/l)	47.90	B	43.30	B	1690000		188.00	
Magnesium (ug/l)	5270.00		4430.00	B	400000		4590.00	B
Manganese (ug/l)	4.20	B	3.50	B	39600		9.00	B
Nickel (ug/l)	9.20	U	9.20	U	1260		9.20	B
Potassium (ug/l)	1760.00	B	1700.00	B	110000		1120.00	B
Silver (ug/l)	4.10	U	4.10	U	54.0		4.10	U
Sodium (ug/l)	3780.00	B	3280.00		19400		2970.00	B
Vanadium (ug/l)	3.60	U	3.60	U	2070		3.60	U
Zinc (ug/l)	48.10		25.60		8760		45.60	
Chloride by IC (mg/l)	4.9				3.7			
Fluoride by IC (mg/l)	0.50	U			0.50	U		
Nitrite by IC (mg/l)	0.25	U			0.25	U		
Nitrate by IC (mg/l)	4.3				0.67			
Phosphate by IC (mg/l)	0.25	U			0.25	U		
Sulfate by IC (mg/l)	18.6				17.9			
Nitrite/Nitrate (mg-N/l)	0.72				0.094			
TOC (mg/l)	3.2				0.96			
pH	8.0				7.2			
Sp. Cond. (umhos/cm)	174				158			
TIC (mg/l)	12.2				16.6			

Site Identification	110-1	Q	110-1	Q	110-1	Q	110-1	Q
Sample Type	seep		seep		seep		seep	
Date	4/1/94		4/1/94		4/1/94		4/1/94	
Time	8:00		8:00		9:45		9:45	
HEIS Sample No.	B0BMJ9		B0BMK0		B0BMK5		B0BMK6	
Filtered/Unfiltered	unfilt.		filt.		unfilt.		filt.	
Quality Control Sample					Dup. B0BMJ9		Dup. B0BMK0	
Aluminum (ug/l)	98.20	B	43.20	B	33.50	B	16.30	U
Antimony (ug/l)	25.40	U	25.40	U	25.40	U	25.40	U
Barium (ug/l)	28.30	B	25.40	B	30.50	B	26.70	B
Beryllium (ug/l)	0.30	U	0.30	B	0.30	U	0.30	U
Cadmium (ug/l)	2.60	U	2.60	U	2.60	U	2.60	U
Calcium (ug/l)	20200.00		20200.00		23600.00		22300.00	
Chromium (ug/l)	24.60		16.00		19.80		20.80	
Cobalt (ug/l)	3.90	U	3.90	U	3.90	U	3.90	U
Copper (ug/l)	17.70	B	17.60	B	16.20	B	3.50	B
Iron (ug/l)	268.00		121.00		100.00		37.70	B
Magnesium (ug/l)	4520.00	B	4480.00	B	5220.00		4940.00	B
Manganese (ug/l)	11.80	B	4480.00	B	4.20	B	4.20	B
Nickel (ug/l)	9.20	U	9.20	U	9.20	U	9.20	B
Potassium (ug/l)	1720.00	B	1460.00	B	1320.00	B	1460.00	B
Silver (ug/l)	4.10	U	4.10	U	4.10	U	4.10	U
Sodium (ug/l)	3100.00	B	3250.00	B	3260.00	B	3410.00	B
Vanadium (ug/l)	3.60	U	3.60	U	3.60	U	3.60	U
Zinc (ug/l)	36.90		46.50		29.20		22.20	
Chloride (mg/l)	2.6				3.8			
Fluoride (mg/l)	0.50	U			0.50	U		
Nitrite (mg/l)	0.25	U			0.25	U		
Nitrate (mg/l)	2.2				3.3			
Phosphate (mg/l)	0.25	U			0.25	U		
Sulfate (mg/l)	14.7				17.2			
Nitrite/Nitrate (mg-N/l)	0.38				0.54			
TOC (mg/l)	1.1				1.1			
pH	8.0				7.5			
Sp. Cond. (umhos/cm)	156				174			
TIC (mg/l)	14.2				14.2			

Site Identification	110-1	Q	110-1	Q	D5-15	Q	D5-15	Q
Sample Type	water		water		groundwater		groundwater	
Date	4/1/94		4/1/94		5/13/94		5/13/94	
Time	11:30		11:30		9:20		9:20	
HEIS Sample No.	B0BMK8		B0BMK9		B0BML1		B0BML2	
Filtered/Unfiltered	unfilt.		filt.		unfilt.		filt.	
Quality Control Sample	blank		blank					
Aluminum (ug/l)	16.30	U	16.30	U	28.7	U	28.7	U
Antimony (ug/l)	25.40	U	25.40	U	33.1	U	33.1	U
Barium (ug/l)	4.50	U	4.50	U	96.6	B	84.5	B
Beryllium (ug/l)	0.30	U	0.30	U	0.20	U	0.20	U
Cadmium (ug/l)	2.60	U	2.60	U	2.9	U	2.9	U
Calcium (ug/l)	652.00	B	764.00	B	71000		62600	
Chromium (ug/l)	3.30	U	3.30	U	1590		1400	
Cobalt (ug/l)	3.90	U	3.90	U	3.3	U	3.3	U
Copper (ug/l)	4.50	B	3.30	U	4.2	U	4.2	U
Iron (ug/l)	35.10	B	20.00	B	34.9	B	16000	
Magnesium (ug/l)	71.50	U	71.50	U	18100		0.90	U
Manganese (ug/l)	2.80	B	3.50	B	1.1	B	7.8	U
Nickel (ug/l)	9.20	U	9.20	U	7.8	U	4470	B
Potassium (ug/l)	887.00	U	887.00	U	5390		5.7	U
Silver (ug/l)	4.10	U	4.10	U	5.7	U	14200	
Sodium (ug/l)	520.00	B	572.00	B	16100		4.1	U
Vanadium (ug/l)	3.60	U	3.60	U	4.1	U	7.2	B
Zinc (ug/l)	22.20		27.70		18.8	B		
Chloride (mg/l)	1.4				22.0			
Fluoride (mg/l)	0.50	U			0.50	U		
Nitrite (mg/l)	0.25	U			0.25	U		
Nitrate (mg/l)	0.25				56.2			
Phosphate (mg/l)	0.25	U			0.25	U		
Sulfate (mg/l)	0.38				101			
Nitrite/Nitrate (mg-N/l)	0.020	U			10.8			
TOC (mg/l)	0.50	U			1.6			
pH	8.2				7.8			
Sp. Cond. (umhos/cm)	1.1				535			
TIC (mg/l)	0.50	U			24.1			

Site Identification	D5-15	Q	D5-15	Q	D8-53	Q	D8-53	Q
Sample Type	groundwater		groundwater		groundwater		groundwater	
Date	5/13/94		5/13/94		5/13/94		5/13/94	
Time	9:25		9:25		12:00		12:00	
HEIS Sample No.	B0BML4		B0BML5		B0BML7		B0BML8	
Filtered/Unfiltered	unfilt.		filt.		unfilt.		filt.	
Quality Control Sample	Dup. B0BML1		Dup. B0BML2					
Aluminum (ug/l)	28.7	U	28.8	B	28.7	U	44.3	B
Antimony (ug/l)	33.1	U	33.1	U	33.1	U	33.1	U
Barium (ug/l)	101	B	90.5	B	70.9	B	79.8	B
Beryllium (ug/l)	0.20	U	0.20	U	0.20	U	0.20	U
Cadmium (ug/l)	2.9	U	2.9	U	2.9	U	2.9	U
Calcium (ug/l)	73800		67000		73300		83300	
Chromium (ug/l)	1650		1500		329		368	
Cobalt (ug/l)	3.3	U	3.3	U	3.3	U	3.3	U
Copper (ug/l)	4.2	U	4.2	U	4.3	B	4.2	U
Iron (ug/l)	29.7	B	4.2	U	21.5	B	9.6	B
Magnesium (ug/l)	18900		17200		10200		11700	
Manganese (ug/l)	0.98	B	0.90	U	1.4	B	0.90	U
Nickel (ug/l)	7.8	U	7.8	U	8.9	B	7.8	U
Potassium (ug/l)	5560		4720	B	3880	B	4430	B
Silver (ug/l)	5.7	U	5.7		5.7	U	5.7	U
Sodium (ug/l)	16900		15300		7880		9010	
Vanadium (ug/l)	4.1	U	4.1	U	4.1	U	4.1	U
Zinc (ug/l)	114		9.6	B	51.0		13.2	B
Chloride (mg/l)	21.9				39.6			
Fluoride (mg/l)	0.50	U			0.50	U		
Nitrite (mg/l)	0.25	U			0.25	U		
Nitrate (mg/l)	56.2				56.8			
Phosphate (mg/l)	0.25	U			0.25	U		
Sulfate (mg/l)	102				115			
Nitrite/Nitrate (mg-N/l)	10.8				10.7			
TOC (mg/l)	1.7				1.1			
pH	7.5				7.2			
Sp. Cond. (umhos/cm)	536				561			
TIC (mg/l)	22.2				17.7			

Site Identification	H4-14	Q	H4-14	Q	H4-11	Q	H4-11	Q
Sample Type	groundwater		groundwater		groundwater		groundwater	
Date	5/13/94		5/13/94		5/13/94		5/13/94	
Time	13:30		13:30		14:22		14:22	
HEIS Sample No.	B0BMM0		B0BMM1		B0BMM3		B0BMM4	
Filtered/Unfiltered	unfilt.		filt.		unfilt.		filt.	
Quality Control Sample								
Aluminum (ug/l)	28.7	U	28.7	U	34.7	B	28.7	U
Antimony (ug/l)	33.1	U	33.1	U	33.1	U	33.1	U
Barium (ug/l)	46.1	B	44.4	B	40.7	B	44.2	B
Beryllium (ug/l)	0.20	U	0.20	U	0.20	U	0.20	U
Cadmium (ug/l)	2.9	U	2.9	U	2.9	U	2.9	U
Calcium (ug/l)	86900		85300		61100		66700	
Chromium (ug/l)	52.6		50.7		64.1		66.3	
Cobalt (ug/l)	3.3	U	3.3	U	3.3	U	3.3	U
Copper (ug/l)	4.2	U	4.2	U	4.2	U	4.2	U
Iron (ug/l)	40.8	B	4.2	U	34.2	B	12.4	B
Magnesium (ug/l)	16700		16400		9010		9850	
Manganese (ug/l)	0.90	U	0.98	U	1.7	B	0.90	U
Nickel (ug/l)	7.8	U	7.8	U	7.8	U	7.8	U
Potassium (ug/l)	5850		5570		3260	B	3340	B
Silver (ug/l)	5.7	U	5.7	U	5.7	U	5.7	U
Sodium (ug/l)	15100		15700		12300		11800	
Vanadium (ug/l)	4.1	U	4.1	U	4.1	U	4.1	U
Zinc (ug/l)	14.8	B	14.4	B	10.8	B	14.4	B
Chloride (mg/l)	6.9				6.3			
Fluoride (mg/l)	0.50	U			0.50	U		
Nitrite (mg/l)	0.25	U			0.25	U		
Nitrate (mg/l)	28.6				28.6			
Phosphate (mg/l)	0.25	U			0.25	U		
Sulfate (mg/l)	143				68.6			
Nitrite/Nitrate (mg-N/l)	5.5				5.2			
TOC (mg/l)	1.9				0.87			
pH	7.6				7.7			
Sp. Cond. (umhos/cm)	557				382			
TIC (mg/l)	--				28.7			

Site Identification	100H	Q	100H	Q	Upriver	Q	Upriver	Q
Sample Type	water		water		river		river	
Date	5/13/94		5/13/94		5/16/94		5/16/94	
Time	16:00		16:00		13:15		13:15	
HEIS Sample No.	B0BMM6		B0BMM7		B0BXG1		B0BXG2	
Filtered/Unfiltered	unfilt.		filt.		unfilt.		filt.	
Quality Control Sample	blank		blank					
Aluminum (ug/l)	28.7	U	28.7	U	39.2	B	28.7	U
Antimony (ug/l)	33.1	U	33.1	U	33.1	U	33.1	U
Barium (ug/l)	2.4	U	2.4	U	27.8	B	26.5	B
Beryllium (ug/l)	0.20	U	0.20	U	0.20	U	0.20	U
Cadmium (ug/l)	2.9	U	2.9	U	2.9	U	2.9	U
Calcium (ug/l)	71.1	B	56.0	B	18300		18300	
Chromium (ug/l)	4.3	U	4.3	U	4.3	U	4.3	U
Cobalt (ug/l)	3.3	U	3.3	U	3.3	U	3.3	U
Copper (ug/l)	4.2	U	4.2	U	4.2	U	4.2	U
Iron (ug/l)	4.2	U	7.0	B	41.0	B	4.8	B
Magnesium (ug/l)	39.6	U	39.6	U	4460	B	4470	B
Manganese (ug/l)	0.90	U	0.90	U	6.3	B	1.3	B
Nickel (ug/l)	7.8	U	7.8	U	7.8	U	7.8	U
Potassium (ug/l)	552	U	552	U	851	B	645	B
Silver (ug/l)	5.7	U	5.7	U	5.7	U	5.7	U
Sodium (ug/l)	180	B	205	B	2420	B	2470	B
Vanadium (ug/l)	4.1	U	4.1	U	4.1	U	4.1	U
Zinc (ug/l)	17.1	B	9.8	B	17.6	B	15.2	B
Chloride (mg/l)	0.25	U			1.3			
Fluoride (mg/l)	0.50	U			0.50	U		
Nitrite (mg/l)	0.25	U			0.25	U		
Nitrate (mg/l)	0.25	U			0.25	U		
Phosphate (mg/l)	0.25	U			0.25	U		
Sulfate (mg/l)	0.25	U			9.9			
Nitrite/Nitrate (mg-N/l)	0.020	U			0.020			
TOC (mg/l)	0.50	U			2.4			
pH	7.8				7.7			
Sp. Cond. (umhos/cm)	2.0				125			
TIC (mg/l)	0.70				11.8			

Site Identification	Composite	Q	Composite	Q	River	Q	River	Q
Sample Type	river		river		water		water	
Date	5/16/94		5/16/94		5/16/94		5/16/94	
Time	15:00		15:00		15:30		15:30	
HEIS Sample No.	B0BMM9		B0BMN0		B0BMN5		B0BXF9	
Filtered/Unfiltered	unfilt.		filt.		unfilt.		filt.	
Quality Control Sample					blank		blank	
Aluminum (ug/l)	51.7	B	34.7	B	28.7	U	28.7	U
Antimony (ug/l)	33.1	U	33.1	U	33.1	U	33.1	U
Barium (ug/l)	26.3	B	26.7	B	2.4	U	2.4	U
Beryllium (ug/l)	0.20	U	0.20	U	0.20	U	0.20	U
Cadmium (ug/l)	2.9	U	2.9	U	3.4	B	2.9	U
Calcium (ug/l)	17300		17500		99.9	B	76.0	B
Chromium (ug/l)	4.3	U	4.3	U	4.3	U	4.3	U
Cobalt (ug/l)	3.3	U	3.3	U	3.3	U	3.3	U
Copper (ug/l)	4.2	U	4.2	U	4.2	U	4.2	U
Iron (ug/l)	46.4	B	24.7	B	6.2	B	4.2	U
Magnesium (ug/l)	4230	B	4310	B	39.6	U	39.6	U
Manganese (ug/l)	6.9	B	1.7	B	0.90	U	0.90	U
Nickel (ug/l)	7.8	U	7.8	U	7.8	U	7.8	U
Potassium (ug/l)	989	B	789	B	552	U	552	U
Silver (ug/l)	5.7	U	5.7	U	5.7	U	5.7	U
Sodium (ug/l)	2400	B	2400	B	158	B	137	B
Vanadium (ug/l)	4.1	U	4.1	U	4.1	U	4.1	U
Zinc (ug/l)	28.2		7.6	B	15.4	B	16.4	B
Chloride (mg/l)	1.4				0.25	U		
Fluoride (mg/l)	0.50	U			0.50	U		
Nitrite (mg/l)	0.25	U			0.25	U		
Nitrate (mg/l)	0.26				0.25	U		
Phosphate (mg/l)	0.25	U			0.25	U		
Sulfate (mg/l)	10.5				0.25	U		
Nitrite/Nitrate (mg-N/l)	0.047				0.020	U		
TOC (mg/l)	2.0				0.50	U		
pH	8.0				7.9			
Sp. Cond. (umhos/cm)	131				1.8			
TIC (mg/l)	12.8				0.50			

APPENDIX B

SOIL TEXTURAL DETERMINATION AND X-RAY DIFFRACTION PROCEDURES

SOIL TEXTURE DETERMINATIONS AND PREPARATION OF SAMPLES FOR MINERALOGICAL ANALYSIS BY X-RAY DIFFRACTION

To disperse soil, weigh 40 g. of soil into a 250-ml plastic bottle, add 30 ml of 0.25 M Na_2CO_3, dilute with deionized water to about 200 ml, and then shake overnight. The next day, remove the bottle from the shaker, separate the sand from the silt and clay by letting the suspension settle for 4 seconds per cm of suspension depth and decanting the suspension through a 53-um-porosity sieve into a large beaker. Resuspend the remaining "sand" in deionized water, let settle for 4 secs/cm and decant through the sieve as before. Finally, transfer all of the sand to the top of the 53-um-porosity sieve and wash the remaining silt and clay through the sieve with deionized water. Dry the sand in an oven, sieve with a nested sieving procedure to separate the different sand fractions. Weigh each fraction and sum to get the sand fraction weight.

To separate the clay and silt fractions, transfer the clay/silt suspension to a large beaker with at least 15 cm of straight wall on the sides and dilute to the 15-cm mark with deionized water. Mix the suspension thoroughly and then let settle for 12 hours. Draw off and save the top 10 cm of suspension using a "J-tube" connected to a vacuum flask, redilute and resuspend the remaining clay/silt solids and let them settle for 8 hours before drawing off the clays as before. Repeat this suspending/settling/drawing off procedure until essentially no clay remains (i.e., the top 10 cm are clear after 8 hours of settling). The soil remaining in the beaker is the silt fraction, that drawn off and saved is the clay fraction. Transfer the silts to a beaker, dry at 60°C and weigh to determine the silt content. Do not dry the clay fraction!

To concentrate the clay fraction, add enough 10 M $MgCl_2$ to flocculate the suspension, let settle (or centrifuge in large plastic bottles to speed up the process) and pour off the clear supernatant. Excess salts may be removed from the flocculated clay by placing the clay in dialysis tubing and soaking in deionized water until a $AgNO_3$ test shows no chloride to be present. The clay fraction weight is determined by the difference between the original soil weight (oven-dry basis) and the sum of the sand and silt fraction weights.

SOIL MINERALOGICAL ANALYSIS BY X-RAY DIFFRACTION

This procedure is designed to provide a semi-quantitative estimate ofthe mineralogical composition of the sand, silt and clay fractions of a soil.

Apparatus

Analyses are performed using a Philips automated powder diffractometer (Model 3520) and Co-K_α radiation. Ordinary random powder sample mounts are used for the sand and silt fractions. Clay fraction samples are mounted on glass slides by the filter-membrane peel technique of Drever (1973) to give preferred orientation and allow estimation of the layer-structure clay minerals by the intensities of their (001) reflections.

Sample Preparation

It is assumed that the soil has been separated into the sand, silt and clay particle-size fractions and has been treated to remove organic matter, carbonates and free iron oxides. For best results, the clay fraction should not be dried, but rather maintained as a flocculated suspension from which aliquots (< 10 ml) are taken for analysis. With a McCrone micronizing grinder or a diamonite mortar and pestle, grind a few grams of the sand and silt fractions to approximately fine-silt size. Prepare duplicate random powder mounts for the sand- and silt-sized fractions using the sample holders provided by Philips.

For the clay-sized fraction, transfer 3 aliquots containing 250 mg of clay into separate 50-ml centrifuge tubes. Add 20-ml of near-boiling 1 N NaOAc (pH 5) to each tube, mix thoroughly and let sit for 5 minutes. To two of the tubes add 3 ml of 10 N $MgCl_2$, and to the other tube add 10 ml of 2 N NaCl. Shake thoroughly to flocculate the clays. Centrifuge until a clear supernatant is obtained and decant the supernatant. Wash the Mg-flocculated clays with 1 N $MgCl_2$, then twice with 1 N $Mg(OAc)_2$ (pH 7), then once more with 1 N $MgCl_2$. Add 1 ml of finely-ground glass wool suspension (see Rich and Barnhisel, 1977) and 5 ml of deionized H_2O. For the Na-flocculated clay, wash twice with 1 N NaCl and then follow the same procedure as for the Mg-flocculated clays, but substitute KCl and KOAc (pH 7) for the Mg salts. The final products are 250-mg subsamples of Mg-saturated (2) and K-saturated (1) clays suspended in deionized H_2O.

To mount the samples for diffraction analysis (Drever, 1973), filter the suspensions onto a 0.47-um porosity, 47-mm diameter triacetate membrane supported by a fritted-glass Millipore filter holder. Invert the filter cake onto a 1/8-inch thick Vycor glass slide and remove air trapped between the clay and the slide by lightly rolling over the top of the membrane a couple times with a 1-inch diameter glass vial. Carefully peel the membrane, leaving the sample on the Vycor slide. Add a few drops of a 10% glycerol solution (in 95% ethanol) to one of the Mg-clay samples on the slide immediately after removing the filter membrane. Allow the ethanol on this slide to evaporate leaving a glycerol-saturated clay. Equilibrate the other two samples overnight in a dessicator at constant relative humidity (30-54% is adequate) until diffraction analysis.

Diffraction Analyses

All diffraction data should be collected by step-scanning (0.05° steps for 2-second intervals is a good combination) and stored on computer for later determination of peak intensities. A simultaneous strip-chart recording of the data will be made for immediate analysis. The qualitative mineralogy of the sand and silt fractions is determined by comparison of the diffraction data with standard patterns in the JCPDS powder diffraction file, using a computerized Johnson-Vand Search/Match algorithm if necessary. To quantify the amounts of each mineral present in the silt and sand fractions, the average mass attenuation coefficient (μ) of each sample is measured. An estimate of the mass attenuation coefficient for each pure mineral phase (μ_p) is also calculated from published values of elemental u values and from assumptions about the composition of the mineral phase in the sample. Direct measurements of μ_p can also be made from standard samples of pure mineral phases. The absolute intensity of the diagnostic peak for each pure mineral phase ($I_p°$) is also measured from standard samples or estimated, if necessary. These values for μ, μ_p, and $I_p°$ are used, together with the observed intensity of the diagnostic peak in the unknown sample (I_p), to calculate the weight fraction of the mineral in the unknown sample (wf) by the following equation:

$$wf = (\mu/\mu_p)(I_p)/(I_p°).$$

The mineralogy of the clay fraction is determined by comparison of the intensities of the (001) reflections after various pretreatments. Because the sum of the weight fractions of all the phases present is equal to 1, it can be shown that

$$\mu = 1/[\text{Sum of } (I_p)/(\mu_p)(I_p°)].$$

Assuming, as a first approximation, that the $I_p°$ values for the layer silicates are identical, the weight fraction of each silicate (wf_{LS}) may then be calculated by the following equation:

$$wf_{LS} = (I_p/\mu_p)(1/[\text{Sum of } (I_p/\mu_p) \text{ for all LS present}]).$$

If no other minerals (e.g., quartz and feldspars) are present in the clay fraction, the wf_{LS} value is the weight fraction of the clay mineral in the sample; otherwise, wf_{LS} pertains only to the weight fraction among the layer silicates in the sample. A more complex equation may be derived to handle situations where non-layer-silicate clay-sized minerals are present in significant quantities. The I_p values are corrected for the Lorentz-Polarization factor and for sample width smaller than the beam width before being used in the weight fraction calculation. As time permits, mass attenuation coefficients and absolute intensities for reference clay minerals will be measured and the first equation can then, hopefully, be used.

Currently, estimates of the illite, kaolinite, smectite, vermiculite and chlorite mineral fractions are made. The following criteria are used to arrive at these estimates:

1) illites are considered to be the fraction that gives 10 Å spacings in Mg-saturated subsamples and does not expand with glycerol treatment;

2) kaolinites are considered to be the fraction that gives 7.2 Å spacings that disappear upon heating to 550°C;

3) smectites are considered to be the fraction of the Mg-saturated subsamples that gives 12-15 Å spacings at 30-54% relative humidity, expands to 17-20 Å upon saturation with glycerol, and collapses to 9-10 Å upon heating to 550°C;

4) vermiculites are considered to be the fraction that gives 12-14 Å spacings in the Mg-saturated subsamples, 10-12 Å spacings in the K-saturated subsamples, does not expand when treated with glycerol, and collapses to 9-10 Å when heated at 550°C.

5) chlorites are considered to be the fraction that gives 14-15 Å and 7-7.5 Å spacings that do not change with either glycerol or heating treatments.

If treatment with ethylene glycol is desired (after the initial analysis of the Mg-saturated subsamples), the slides that have not received the glycerol treatment may be equilibrated in a desiccator containing free ethylene glycol at about 60°C for a minimum of 1 hour, preferably overnight. As discussed by MacEwan and Wilson (1980, p.222-226), however, glycerol saturation provides a better separation of the vermiculite and smectite phases than saturation with ethylene glycol. The glycolated samples are then analysed as before to distinguish between the smectite and vermiculite fractions. The K-saturated samples, following the initial analysis, should be heated to 575°C for 1 hour before being re-analysed to distinguish the chlorite from the kaolinite fractions.

The net result of this procedure should be a minimum of four x-ray patterns corresponding to clays that are Mg-saturated, Mg-saturated + glycerol (or glycol), K-saturated, and K-saturated + 575°C heat. Interpretation of these four patterns will allow distinction among the five clay mineral groups listed above.

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