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CADMIUM GEOCHEMISTRY IN SOIL AND GROUNDWATER AT THE F AND H SEEPAGE BASINS (U)

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MASTER

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EXECUTIVE SUMMARY

For 33 years, low activity liquid wastes from the chemical separation areas at the U. S. Department of Energy's Savannah River Site were disposed of in unlined seepage basins. This disposal practice was discontinued in 1988. At that time, the basins were drained and a low permeability cover system was placed over the basins. In the summer of 1993, soil and associated pore water samples of widely varying groundwater chemistries and contaminant concentrations were collected from the region downgradient of these basins using cone penetrometer technology. Analysis of these samples using inductively coupled plasma - mass spectrometry has allowed the investigation of cadmium partitioning between the aqueous phase and soil surfaces at this site. The distribution of cadmium was examined with respect to the solution and soil chemistry (e.g., pH, redox potential, cation and contaminant concentration) and aqueous-phase chemical speciation modeling.

Cadmium was detected in 35 of 53 aqueous samples from the F- and H-Area Seepage Basins (FHSB). Porewater concentrations were found to vary from 0.48 to 23.5 $\mu g\ l^{-1}$, with a mean concentration of 3.1±4.3 $\mu g\ l^{-1}$. Based on the 43 of 86 soil samples for which cadmium was detected, the concentration in the soil ranged 88.5 to 1090 $\mu g\ kg^{-1}$. The mean soil concentration was 214±168 $\mu g\ kg^{-1}$. This concentration is not significantly different from the concentrations observed in two upgradient soil samples collected from the same lithologic unit. The concentrations from these samples were 293±214 and 431±293 $\mu g\ kg^{-1}$.

Field-observed distribution coefficients calculated for 18 sample sets varied from 5.4 to 580 $l\ kg^{-1}$. Based on laboratory studies, little or no cadmium is expected to be sorbed by the soil at pH values less than 4.5. In these experiments, cadmium was actually released from the soil matrix at low aqueous pH values. The K_d value of six used in the previous groundwater modeling effort (GeoTrans, 1991) is in fairly good agreement with the best fit K_d from the field-derived sorption data of 13.

As pH increases above 4.5, the amount of cadmium sorbed by the soil shows a gradual increase. Laboratory data of the leaching of cadmium from background soils using a simulated low-pH waste solution suggests that the cadmium observed in the groundwater downgradient of FHSB is the result of acidic leaching of cadmium from the natural mineral phases. Based on these observations of increased sorption and decreased leaching which occurs as the groundwater pH increases, cadmium concentrations are expected to naturally decrease below the Ground Water Protection Standard in the Watertable Aquifer.

Experiments conducted into cadmium binding to dissolved organic matter show that, as reported by other researchers, the binding of cadmium to DOM is pH dependent and the amount bound increases with increasing pH. Experimental and modeling results of DOM-cadmium interactions, a process which could increase the aqueous phase concentrations of cadmium, is not expected to be important during remediation.

Keywords: sorption, speciation, geochemistry, cadmium, F and H Seepage Basins

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1.0 INTRODUCTION

To properly assess the risk associated with a waste site and to accurately assess potential remedial alternatives, knowledge of contaminant concentrations and the geochemical transport characteristics of each contaminant is required. Contaminants that are soluble in water may not travel through the subsurface environment at the same velocity as the water due to the processes of solid-phase sorption and precipitation. Therefore, to accurately predict contaminant transport, a knowledge of both aqueous-phase and solid surface speciation is necessary.

This study has been designed to determine contaminant concentrations, and to generate site-specific transport factors for contaminated soil and groundwater downgradient of the F and H Area Seepage Basins (FHSB). This report describes the results of this study for cadmium. In particular, this report addresses the following subjects:

- quantification of the amount of cadmium in the soil (i.e., the soil source term);
- a description of the aqueous-phase speciation of cadmium in groundwater at the basins;
- an investigation of the geochemistry controlling the partitioning of cadmium between the groundwater and soil surfaces at the basins;
- laboratory studies of the leaching of cadmium from background (unimpacted) soils; and
- an investigation into the binding of cadmium to dissolved organic matter.

The basic experimental approach in this study was to collect soil and its associated porewater from contaminated areas downgradient of the FHSB. Samples were collected over a wide range of geochemical conditions (e.g., pH, conductivity, and contaminant concentration) and were used to describe the partitioning of contaminants between the aqueous phase and soil surfaces at the site. The partitioning behavior can then be used to develop defensible site-specific transport factors.

The site-specific transport factors derived from this study can be used to update the current flow and transport models in order to better evaluate remedial alternatives and calculate risk levels at this site.

This report is organized as follows:

- Section 1 is the introduction including the waste site background, risk drivers, and a conceptual hydrogeochemical model of the site;

- Section 2 describes the experimental approach taken to collect data on the geochemistry of the FHSB;
- a mathematical description of the models employed for aqueous-phase and surface-sorption processes, as well as the binding of cadmium to dissolved organic matter is presented in Section 3;
- the results of field and laboratory analytical data and the calculations and modeling used to evaluate the geochemistry at the FHSB are contained in Section 4;
- Section 5 contains a summary of data and conclusions; and
- descriptions of on going work and recommendations from this study are presented in Section 6.

1.1 Waste Site Background

From 1955 until 1988, the FHSB received process waste water and storm-water runoff from the tritium and plutonium separation facilities at the Savannah River Site in South Carolina. The unlined basins were designed to allow the natural processes of evaporation and infiltration to dispose of the polluted effluent streams. This has resulted in groundwater in the vicinity of these basins exhibiting a lower pH and elevated concentrations of metals, radionuclides, nitrate, and sodium as compared to background water quality.

On November 7, 1988, discharge to the basins was terminated in accordance with requirements of Resource Conservation and Recovery Act. Before a multi-layered cap was placed over the basins, the liquid was removed and each was filled with a gravel bed topped with layers of calcium carbonate and blast furnace slag. The carbonaceous rock was intended to raise the pH of the naturally infiltrating rainwater to a pH of between 8 and 9, while the slag, a source of reduced iron and sulfides, was intended to lower the redox potential of the water. Under these conditions of high pH and low Eh, heavy metals were expected to precipitate from solution (Closure Plan for the F-Area Hazardous Waste Management Facility, WSRC, Aiken, SC).

1.2 Constituents of Concern and Risk Drivers

The constituents of concern for the FHSB as determined in the baseline CERCLA risk assessment are presented in Table 1-1, along with the partitioning coefficients used in groundwater modeling for the waste unit (GeoTrans 1991).

Table 1-1. Distribution coefficient values (K_d) currently used in groundwater modeling of F- and H-Area contaminants of concern. Adapted from Looney (1985).

Contaminant	Typical value for SRS	Range of reported values
Inorganics		
Aluminum	5[1]	Not reported
Arsenic	3	1 - 10
Barium	5[1]	530, 2800
Cadmium	6	1 - 900
Chromium	40	1 - 1000
Copper	25	1 - 100
Fluoride	0.001	Not reported
Iron	5[1]	Not reported
Lead	100	1 - 10,000
Manganese	5[1]	Not reported
Mercury	15[1]	10,000 - 1,000,000
Nickel	100	10 - 1000
Nitrate	0.001[1]	Not reported
Selenium	2.5	1 - 100
Silver	100	10 - 100
Zinc	16	0.1 - 10,000
Organics		
Cyanide	0.01	Not reported
Phenol	0.003[1]	Not reported
C_2Cl_4	0.022	Not reported
Radionuclides		
Cs-137	500	10 - 100,000
Cm-243	3000	100 - 100,000
H-3	0.001	0.000001 - 0.001
I-129	0.2	0.001 - 1
Ra-226	100	10 - 1,000,000
Ra-228	100	10 - 1,000,000
Sr-90	8	1 -1000
Th-228	100	10 - 100,000
U-234	40	0.1 - 1,000,000
U-238	40	0.1 - 1,000,000

[1]"Best guess" value per personnel communication between GeoTrans, Inc. and David Nix of WSRC.

Risk associated with the FHSB was evaluated in the Remedial Alternative Risk Assessment for the F- and H-Area Seepage Basins Groundwater Unit (WSRC 1992a). The results of this analysis for the "no action" alternative are summarized in Tables 1-2 to 1-5. All risk levels were taken from the ingestion of groundwater by a hypothetical on-site resident and the long-term drivers were evaluated at the 100 and 1000 year time step. Although cadmium was not predicted to be a significant risk contributor in this analysis, it has been observed above the regulatory maximum contaminant level (MCL) (see Figures 1-1 and 1-2).

Table 1-2. F-Area Carcinogenic Risk

	Present		100 Year		1000 Year	
Constituent	Risk	% Tot	Risk	% Tot	Risk	% Tot
Uranium-238	5E-3	66	4E-3	80	1E-3	80
Uranium-234	7E-4	10	6E-4	10	3E-5	10
Radium-228	2E-4	4	2E-4	8	3E-5	10

Source: Remedial Alternative Risk Assessment for the F- and H-Area Seepage Basins Groundwater Unit (WSRC 1992a).

Table 1-3. F-Area Noncarcinogenic Risk

	Present		100 Year		1000 Year	
Constituent	Haz Ind	% Tot	Haz Ind	% Tot	Haz Ind	% Tot
Lead	1000	99	1100	99	1100	99
Manganese	80	LT 1	30	LT 1	10	LT 1
Copper	20	LT 1	20	LT 1	10	LT 1
Mercury	10	LT 1	10	LT 1	10	LT 1

Source: Remedial Alternative Risk Assessment for the F- and H-Area Seepage Basins Groundwater Unit (WSRC 1992a).

Table 1-4. H-Area Carcinogenic Risk

	Present		100 Year		1000 Year	
Constituent	Risk	% Tot	Risk	% Tot	Risk	% Tot
Strontium-90	5E-4	40	2E-5	2	1E-7	0
Radium-226	5E-4	40	5E-4	50	5E-4	99
Iodine-129	1E-4	10	9E-5	10	LT E-8	0
Tritium	9E-5	10	LT E-8	0	LT E-8	0

Source: Remedial Alternative Risk Assessment for the F- and H-Area Seepage Basins Groundwater Unit (WSRC 1992a).

Table 1-5. H-Area Noncarcinogenic Risk

	Present		100 Year		1000 Year	
Constituent	Haz Ind	% Tot	Haz Ind	% Tot	Haz Ind	% Tot
Lead	1000	99	5000	96	5000	96
Copper	5	LT 1	100	2	90	2
Mercury	100	1	90	2	90	2

Source: Remedial Alternative Risk Assessment for the F- and H-Area Seepage Basins Groundwater Unit (WSRC 1992a).

1.3 Conceptual Hydrogeochemical Model

Attempts to select an appropriate remediation technology for groundwater at this site have been hampered by an inability to adequately predict the transport of pollutants through, and the amount of contaminants in, the subsurface environment. The models currently being utilized for risk assessment use single literature reported or "best guess" K_d values. Because little data existed for the concentrations and distribution of contaminants in the solid phase (i.e., in the soils), "best guess" K_d values were used to calculate the soil concentration of contaminants based on observed groundwater concentrations (GeoTrans 1991). Therefore, these models predicted very large source terms for constituents with high K_d values and that these contaminants should be sorbed by the soil and not substantially transported (GeoTrans 1991; WSRC 1992a). In actuality, soil cores collected from directly beneath the basins (Corbo, et. al. 1985) contained much lower concentrations of many contaminants than was predicted by the models and significant groundwater transport of some contaminants (e.g. cesium, lead, mercury) from the site has been observed (WSRC 1992b; WSRC 1992c), although little transport was predicted.

This apparent failure of model predictions using literature K_d values stems largely from the fact that the geochemical conditions downgradient of the basins are (1) much different (low pH and high ionic strength) than the conditions under which the literature K_d values were determined and (2) the operations of the basins has significantly altered the soil surfaces by stripping and/or precipitating surface mineral coatings.

The waste discharged to the FHSB was generally acidic with a high salt concentration. Typically, waste solution pH values were approximately 2.6 with NO_3^- and Na^+ concentrations of 880 ppm and 400 ppm respectively (Ryan 1984). Under these conditions, the soil coatings and matrix are expected to be highly altered. This is especially true of the very fine, high surface area clay fraction. X-ray diffraction analysis of the < 2 μm fraction of several samples collected in this study show that clay fraction of soil in the vicinity of FHSB is primarily kaolinite [$Si_4Al_4O_{10}(OH)_8$] (Johnson 1994). The iron oxides hematite [Fe_2O_3] and goethite [FeOOH] are present as surface coatings on these soils leading to the typical reddish-brown coloration. Dissolution of the soil coating and matrix is evident from changes in the groundwater chemistry as it flows away from the basins. Downgradient of the basins, the pH of the system has increased as the concentration of H^+ ions in the acidic waste water has been replaced by Al^{3+}, Si^{4+}, Fe^{3+}, Na^+ ions from the soil matrix.

As groundwater concentrations of common soil matrix ions and the pH increase, precipation of new minerals is expected to occur. Based on thermodynamic speciation modeling (discussed in greater detail below), groundwater downgradient of the FHSB is currently overstaturated with respect to several types of Si, Fe, and Al based minerals and oxides. The precipitation of these mineral phases is expected to occur on the surface of the existing soil surfaces, resulting in the formation of new reactive surface coatings. These new coatings will, therefore, influence future binding of contaminants in the plume.

1.4 Dissolved Organic Matter

This section describes work completed with assistance from the National Science Foundation Summer Undergraduate Research Program and the Savannah River Ecology Laboratory to develop thermodynamic stability constants for the binding of cadmium (II) ions to naturally occurring dissolved organic matter (DOM).

DOM is ubiquitous in natural waters, and its effect on the chemistry and biology of these systems has been the subject of much recent research. Relative to other dissolved solutes, its abundance is second only to bicarbonate for all dissolved constituents in the "world average river" (Schlesinger and Melack 1981). In spite of their occurrence and abundance, there still exists a fundamental lack of understanding about the way these compounds affect the chemistry of natural waters. Much of this lack of knowledge arises from the problems associated with the analytical description and conceptual difficulties of understanding the highly complex mixture of organic compounds that make up naturally occurring DOM.

The actual mobilization and transformation processes that result in DOM formation are still not well understood, although it is believed that DOM is formed from the mobilization of decomposing dead organic matter by percolating rainwater (Beck et al., 1974) and/or by the polymerization of polyphenols, amino acids, and carbohydrates that were derived from decaying organic matter (Beck et al. 1974; Wetzel 1975). Thurman (1985) has suggested that, in general, biologically labile carbohydrates are oxidized, resulting in organic matter having an increased carboxyl group content.

The complicated processes by which DOM is formed account for the large number and the diverse nature of organic compounds that make up the DOM pool. From a conceptual standpoint, some researchers have completely failed to treat DOM as a mixture of compounds, but rather have attempted to describe this mixture as a small number of simple compounds with their associated physical constants (Sposito and Holtzclaw 1977; Sposito et al. 1977). The treatment of DOM as a small number of simple compounds cannot be a valid chemical representation, because only several percent of the organic carbon content of the DOM can be accounted for by simple pure compounds (i.e., there exist a very large number of organic compounds in the DOM pool and all are at low concentrations). The complex mixture nature of DOM is confirmed by the results of spectrophotometric methods (Wilson et al. 1987; Preston and Schnitzer 1984) and potentiometric titrations (Sposito and Holtzclaw 1977; Sposito et al. 1977; Cabaniss and Shuman 1988a; 1988b) of DOM samples which exhibit no distinct peaks or inflections such as those typical of the analysis of single pure compounds.

Even though chemical analyses of DOM often lack much of the specific chemical information usually present in the analysis of single compounds, certain generalizations regarding the bulk chemical properties of DOM can be made. With oxygen contents typically between 35 and 45 percent and nitrogen and sulfur contents between 1 and 2 percent and less than 1 percent (by weight), respectively (Thurman 1985), the chemistry of

these materials tends to be dominated by the reactivity of their oxygen-containing functional groups. More specifically, these oxygen containing functional groups have been shown to bind protons and metal ions, thereby, significantly affecting the acid-base and metal-speciation chemistry of natural waters (Hemond 1980; Cronan et al. 1978; Cabaniss and Shuman 1988a; Reuter and Perdue 1977). The average pK_a, the pH where one-half of the acidic sites are protonated, for DOM is around 4 for the "strong acids" component (roughly corresponding to the carboxyl groups) and around 10 for the "weak acids" (roughly corresponding to phenols, enols, and sugars). These materials, therefore, are sufficiently acidic to influence the acid-base chemistry of natural waters. Their impact is most pronounced in waters that are either poorly buffered or have high dissolved organic carbon (DOC) concentrations (Sullivan et al. 1989; and Cantrell et al. 1990).

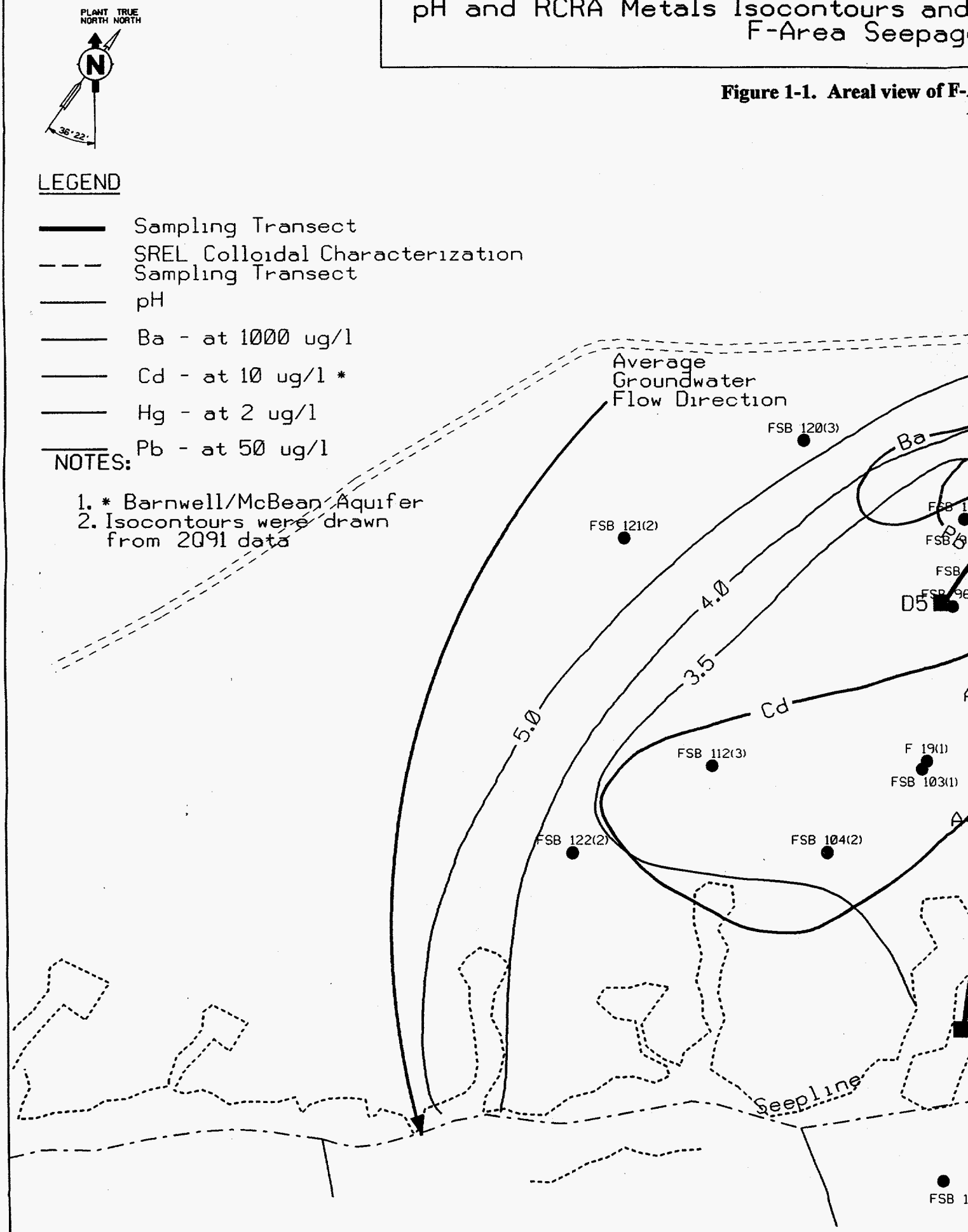
The most obvious effects of DOM on water chemistry are the abilities of DOM to alter the acid-base chemistry and metal speciation of these systems. By taking part in regulating the concentration and speciation of metals, DOM has a direct impact on nutrient availability and metal toxicity for aquatic biota (Erikson et al. 1970; Gachter et al. 1973; Kaiser 1980; Stiff 1971; Sunda and Guillard 1976). Furthermore, the need to predict the transport of metal pollutants in the environment has necessitated that the effect of DOM on the speciation of these metals be evaluated. Recent attempts at predicting metals speciation and transport in ground and surface waters (e.g., the USEPA's MINTEQA2) have neglected the effects of DOM-metal binding or have modeled these compounds as simple organic ligands. As a result, these metal speciation and transport models have been of limited utility in systems where DOM is a significant component.

Although there exists much data on the binding of metals to naturally occurring DOM (Buffle et al. 1977; Reuter and Perdue 1977; Shuman and Woodward 1977; Shuman and Michael 1978; McKnight and Morel 1979; Shuman and Cromer 1979; Mantoura 1981; McKnight 1981), the current state of knowledge in this area is largely an empirical description of metal and proton binding processes. The empirical description of metal binding has, to this point in time, been treated by the use of conditional stability constants. The concept of conditional stability constants is that the equilibrium "constant" obtained from an experiment is applicable only for the experimental conditions under which the data were collected. The experimental conditions (e.g., factors which affect the value obtained for the conditional stability constant) include:
(1) pH; (2) ionic strength; (3) temperature; and (4) the character of the organic ligands.

At the FHSB, since the closure of the basins dissolved organic carbon concentrations (as measured by the total organic carbon analysis) have averaged about 1 ppm carbon or about 2 ppm organic matter with maximum observed concentrations of 8.9 and 14.0 ppm carbon for the F and H Areas respectively (Boltz 1992). In relatively dilute groundwater systems, concentrations in this range can significantly influence metal speciation. Furthermore, because the solubility of naturally occurring DOM increases with increasing pH (Thurman 1985), higher DOM concentrations are expected as the pH of the groundwater system at the FHSB returns to more neutral conditions.

pH and RCRA Metals Isocontours and
F-Area Seepag

Figure 1-1. Areal view of F-



Sampling Transect Locations Basins

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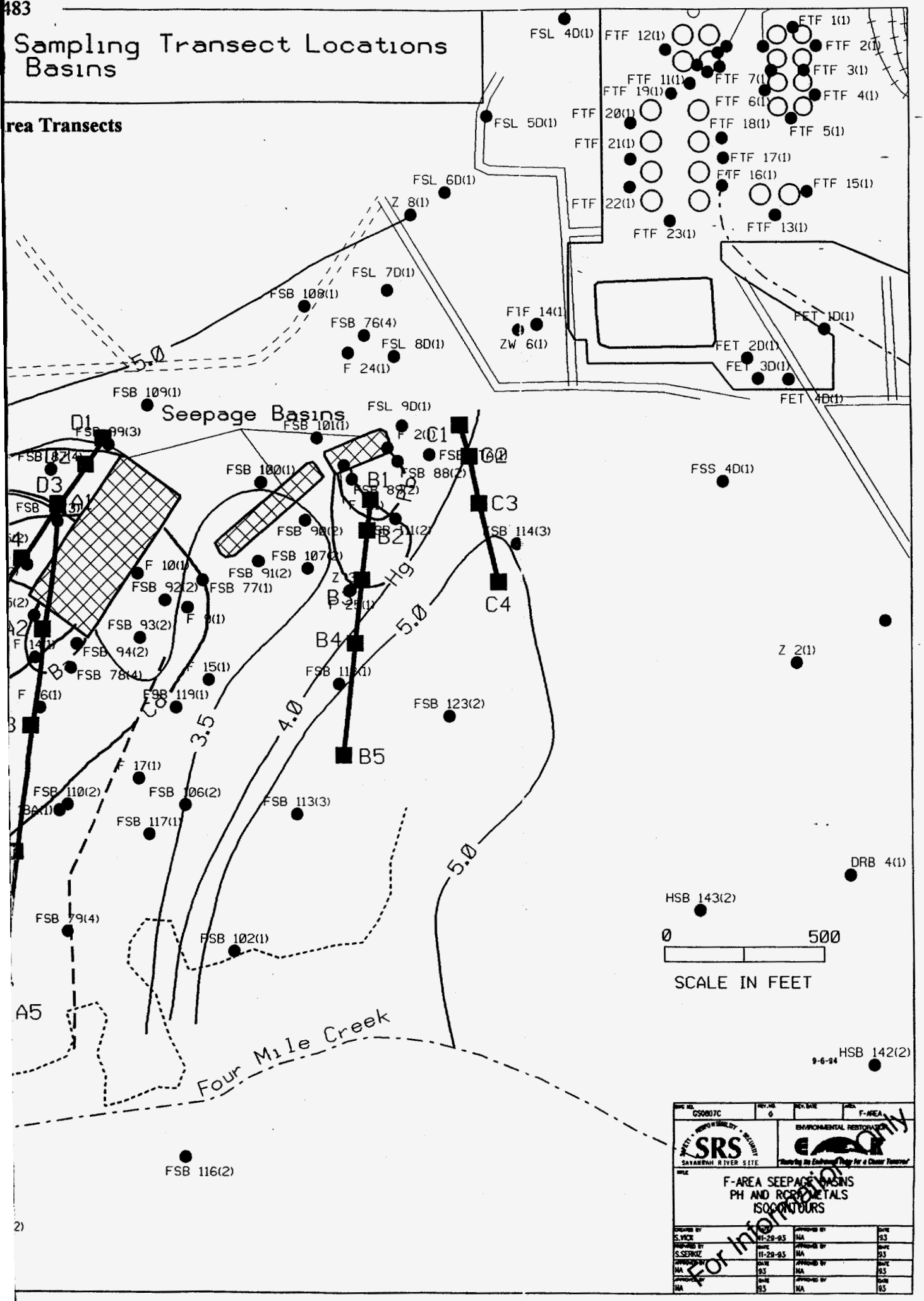


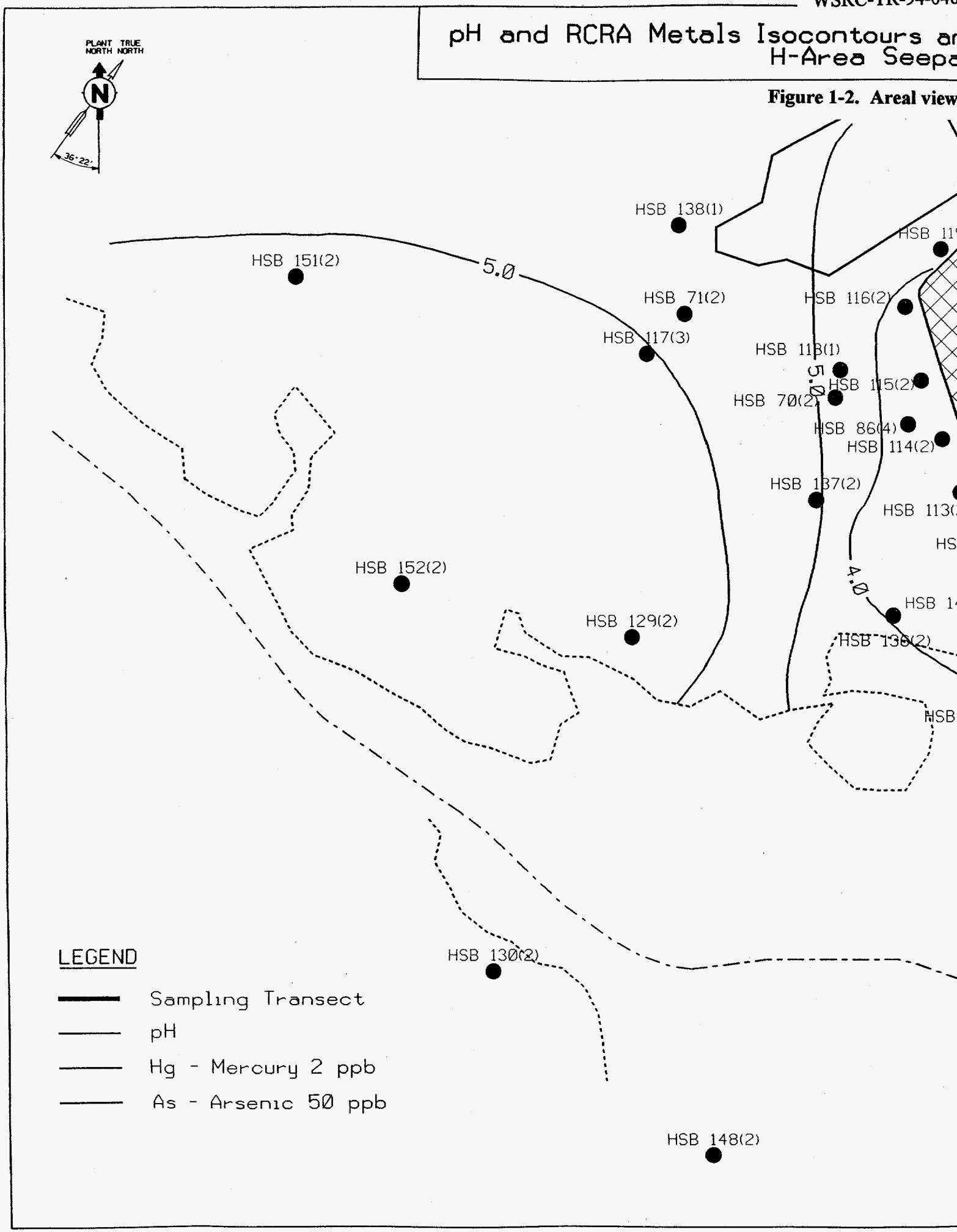
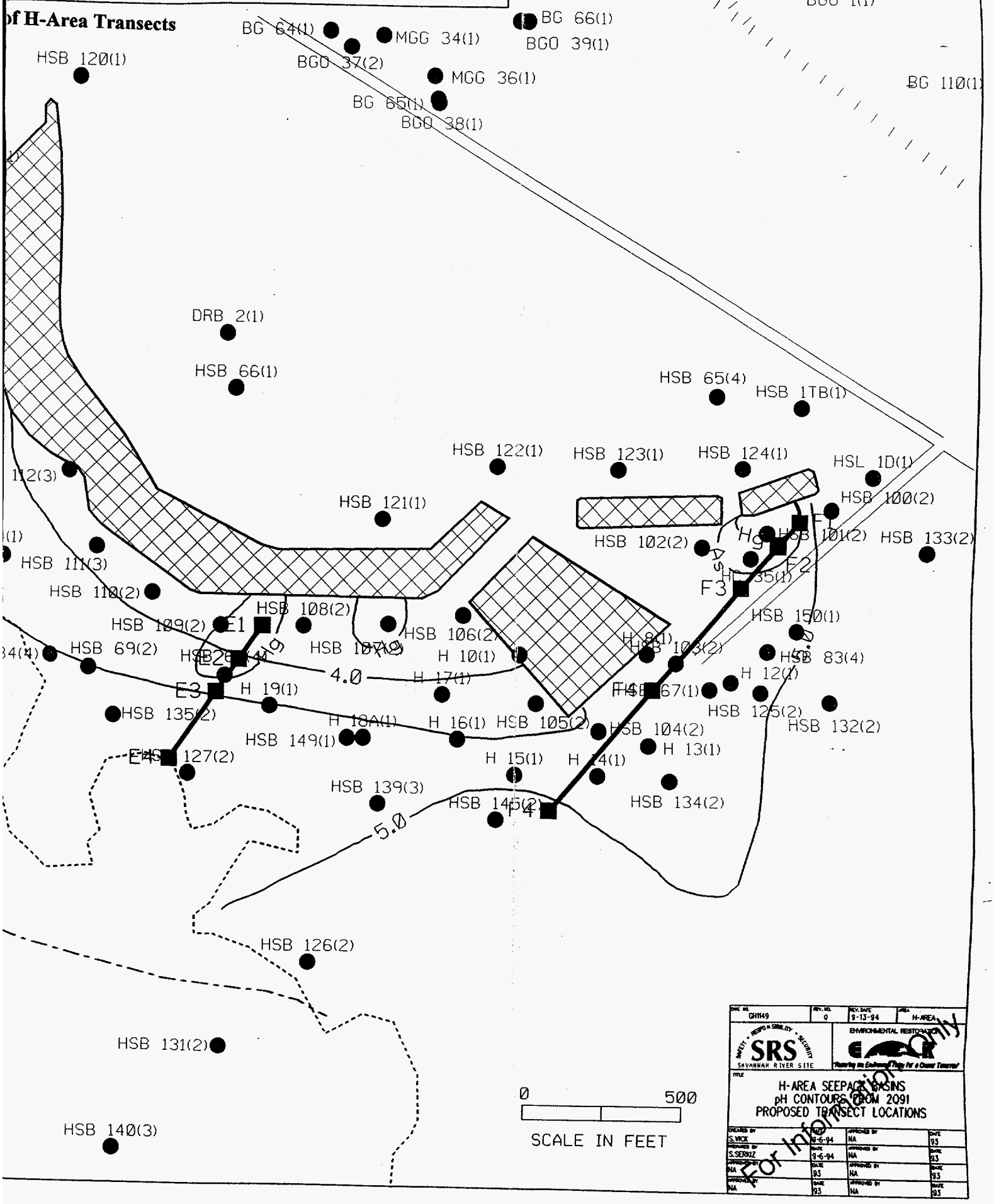


Figure 1-2. Areal view

d Sampling Transect Locations
ge Basins

of H-Area Transects



2.0 EXPERIMENTAL APPROACH

The basic experimental approach in this study was to collect soil and its associated porewater from contaminated areas downgradient of the FHSB. Samples were collected over a wide range of geochemical conditions (e.g., pH, conductivity, and contaminant concentration) and were used to describe the partitioning of contaminants between the aqueous phase and soil surfaces at FHSB. The intent was that the partitioning behavior of each contaminant could be used to develop defensible site-specific transport factors for use in transport modeling of the waste unit.

2.1 Sampling

A total of 52 sets of soil and porewater samples and 32 vadose zone soil samples were collected for this study. Samples were collected using an electric friction-cone penetrometer system with a hydrocone (Edge and Cordy 1989) or geocone depending on the media to be sampled. All hydrocone porewater samples were collected under a constant backpressure applied with argon. The argon gas ensured inert conditions were maintained until the sample was drawn to the surface. Samples sets (i.e., soil and its associated porewater) from the saturated zone downgradient of the waste sites were collected from the same depth, at the same location. Replicate samples (i.e. saturated zone sample pairs and soil samples from the vadose zone) were collected at ten percent of the sampling locations selected on a random basis.

Sampling locations and depths were selected such that they spanned a range of groundwater pH (pH=3-7) and major ion chemistries, and had previously exhibited groundwater contaminant concentrations above the analytical detection limits. The areal view of the sampling transects, along with pH and RCRA metals isoconcentration contours are shown in Figures 1-1 and 1-2 for the F and the H Areas respectively. The cross sections for each of these sampling transects are shown in Figures 2-3 through 2-8 for transects A through F, respectively.

All samples collected in the field were identified by a 4 digit sample identification number. The first letter in a sample name (A-F) represents the transect from which it came. The second number (1-5) is the hole in the transect, whereas the third number (1-4) is the relative sampling depth from which the sample came. The forth digit represents the type of sample; 'S' for soil, 'W' for water. For instance, sample C42W is a water sample from the second depth (48 feet) at CPT location C4. Table 2-1 lists site coordinates of CPT sampling locations and depths of all samples.

Two uncontaminanted background soil samples representative of the same lithographic unit sampled downgradient of the FHSB were collected from the Little Grand Canyon area which is upgradient of F-Area. The soils were collected from the near surface at an outcropping height of approximately 20 feet above the tan clay layer. This depth is lithologically equivalent to that where the deeper samples were collected for this work.

These samples were given the designation GC4 and GC5. Both samples were characterized in terms of their physical and chemical properties.

2.2 Analysis

Immediately upon obtaining water samples in the field, temperature, pH, redox potential, and conductivity of the sample were measured. Temperature and pH were measured using a pH meter with a built in temperature monitor. Redox potential was measured directly using a combination platinum electrode. Porewater samples were stored in acid-washed 1-l LDPE bottles. Soil samples were double bagged into 4-l zip-lock bags. Both porewater and soil samples were then stored in a cooler on ice until the end of the day. After Health Protection personnel verified that the beta and gamma count rates were not above background levels, the samples were transported to a dark sample storage cooler which was temperature regulated at 4°C.

Within a week of sampling, two 10-ml aliquots of each porewater sample were filtered using 0.45 µm syringe filters. Both of these aliquots were analyzed for ^3H using liquid scintillation counting and Cl^-, F^-, NO_2^-, NO_3^-, PO_4^{3-}, and SO_4^{2-} concentrations using ion chromatography. A 60-ml aliquot of the sample was analyzed for organic and inorganic carbon using an automated carbon analyzer.

The remaining sample was filtered through a 0.45 µm cellulose nitrate membrane and acidified to 1% v/v with 70% ultra-pure HNO_3. The acidified samples were analyzed quantitatively using inductively coupled plasma (argon) mass spectrometry (ICP-MS) for 43 isotopes representing 28 elements. Additionally, a semi-quantitative ICP-MS scan for the isotopes of Hg and the actinides (mass less than 246) was also performed. 500 ml of the acidifed sample was placed in a 1-l Marinelli beaker for analysis by gamma spectrophotometry.

Physical and chemical properties of the soil samples examined, including total digestion elemental analysis, soil pH, particle size distribution, carbon content, cation exchange capacity, and hygroscopic moisture content. Additionally, gamma spectrophotometry was performed on a 200 cm^3 aliquot of most samples.

Each soil sample was prepared for total digestion elemental analysis using the hydrofluoric acid digestion procedure outlined by Lim (1982). Samples were prepared in triplicate by digesting approximately 200 mg of soil in 1 ml of ultra-pure aqua regia and 10 ml of ultra-pure HF. Samples were then heated in a digestion bomb at 100°C for 3 hours, filtered through 0.45 µm Teflon filters, and diluted to 50 ml with deionized water. After ICP-MS analysis, as outlined above, contaminant concentrations in the total digestion extract were converted to soil concentrations by multiplying by a conversion factor equal to the extract volume divided by the digested sample weight.

Particle size analysis of each soil sample was performed using the method presented by Gee (1986). Two 40-g aliquots of each sample were prepared for analysis by removing surface coatings and cementing agents. Dispersion of the soil particles was facilitated by shaking the soil overnight in a sodium hexametaphosphate solution. The distribution of the sand fraction (>53 μm) of each sample was determined by passing the dispersed sample through a series of brass sieves. All soil particles which passed through the smallest (53μm) sieve were analyzed to determine amount and size distribution of the silt (2 - 53 μm) and clay (<2 μm) fractions using a pipet-sedimentation method. Data from the two replicates was averaged to obtain the sand, clay and silt fractions.

The cation exchange capacity of each soil sample was measured in duplicate using the barium-magnesium exchange technique described by Rhoades (1982). A 2-g portion of soil was saturated with barium by equilibration with a $BaCl_2$ solution at pH of 4.5. The soil was then reacted with $MgSO_4$ which results in the replacement of the sorbed Ba with Mg. The amount of Mg sorbed per unit weight of soil is equivalent to the cation exchange capacity and is reported in meq kg^{-1}.

Soil pH was determined in using ASTM procedure D4972-89 (ASTM 1989).

ICP-MS allows the determination of elemental concentrations of up to 70 elements at ng l^{-1} concentrations with minimal sample volume. The analysis method uses a plasma torch to ionize the sample by heating it to 8000°K. The cations are drawn through a low vacuum interface into a mass spectrometer which determines the isotopic concentration by the charge to mass ratio of the cations. Elemental concentrations can then be calculated by correcting for the natural abundance of an isotope and the ability of an element to be ionized. Interferences occur at atomic mass numbers where two or more elements have isotopes or masses where doubly ionized atoms are present. Prior to analysis, each sample, standard, or blank, was spiked with a series of elements at known concentrations. Based on counts obtained from these internal standards, calculated concentrations are normalized to account for instrument response changes.

Because the instrument is designed to detect individual atoms rather than solution activity or number of atoms decaying, the detection limit of ICP-MS is outstanding for metals and long-lived radionuclides. Many elements may be analyzed for by monitoring more than one isotope. The detection limit for a given element was determined daily. It is influenced by the alignment and sensitivity of the instrument, the background counts and natural isotopic abundance of the isotope being examined, and ionization potential of the element. In this study, instrument response to cadmium concentration was linear over the entire quantification range (0.05 - 500 μg l^{-1}). The minimum detectable level was assumed to be equal to one-half the minimum standard concentration which varied from 0.05 to 1.5 μg l^{-1}. Results of individual samples were examined for large standard deviations based on three or more analyses of a given sample replicate.

Two of the eight stable cadmium isotopes, ^{111}Cd and ^{114}Cd, were analyzed for using ICP-MS. The concentrations obtained for each of these isotopes were corrected for their

natural isotopic to yield the total elemental cadmium concentration. The total concentration values based on both isotopes were averaged to determine the total cadmium present. Distribution coefficients for each sample were calculated by dividing the soil concentration of an isotope (in $\mu g\ kg^{-1}$) by the concentration of that element or isotope in the associated porewater sample (in $\mu g\ l^{-1}$). No distinction was made between anthropogenic and naturally occurring cadmium. This could result in an over-estimation of reported in-situ K_d values as cadmium concentrations associated with the soil matrix are included in the reported soil concentration.

2.3 Laboratory Studies of Cadmium Binding to Background Soils

Laboratory studies examining the sorption of cadmium to FHSB soils are currently being conducted. The first of these studies is a batch sorption study. In it, 1.00 g of upgradient soil is allowed to react with 42 ml of $CdNO_3$ solution in a 50 ml HDPE Oak Ridge tube. After shaking at 25°C for a specified period of time, the mixture was centrifuged at 10,000 g for 10 minutes. The supernate was then decanted and filtered through a 0.45 μm cellulose nitrate membrane and acidified to 1% v/v with 70% ultra-pure HNO_3. The initial and equilibrium solution pH was measured. The fraction of cadmium sorbed by the soil was determined by comparing the initial mass of cadmium in solution to the mass present after equilibration. Cadmium concentrations were measuring using inductively coupled plasma - emission spectroscopy (ICP-ES).

Two types of sorption batch studies have been performed with cadmium. The first study examined the kinetics of cadmium sorption to SRS soils. The pH of a 10^{-5} M $CdNO_3$ solution was adjusted to an initial value of 3.0, 3.9, 5.3 or 10.5. Tubes containing the soil/water mixture were allowed to react for varying times to determine the time necessary to reach equilibrium. The second type of batch study examined the effects of pH and cadmium concentration on sorption. Tubes containing solutions with $CdNO_3$ concentrations of 10^{-4}, 10^{-5}, and 10^{-6} M, were pH adjusted over a range of 3 to 8 and allowed to equilibrate overnight with the soils.

The second laboratory study will examine the influence of modifying soil surfaces on sorption behavior. For this work, approximately 8 kg of an uncontaminated soil collected upgradient of the FHSB, were packed into a column. Then, 100 l (equivalent to approximately 39 pore volumes based on soil weight and column geometry) of deionized water were allowed to pass through the column at an average flow of about 6 pore volumes per day. The influent and effluent from the column was sampled and analyzed using ICP-ES and ICP-MS to determine the aqueous chemistry of the weathering process.

A simulated FHSB waste solution was then passed through the column to allow the background soil to undergo a weathering process similar to that of the FHSB soils. The simulated waste solution has a pH of 2.5 with 1000 ppm NO_3^- and about 300 ppm Na^+. In future work, a portion of the soil will be periodically

removed and batch cadmium sorption studies conducted on it. This experiment will allow a comparison of the sorption behavior of modified soil as a function of waste solution volume.

2.4 Binding to Dissolved Organic Matter

If environmentally representative models are to be developed for the acid-base and metal speciation chemistry of surface and ground waters, the effects of DOM on the chemistry of these waters must be evaluated.

This portion of this study is intended to describe, in a predictive manner, the effects of DOM on cadmium speciation. This characterization was carried out over an environmentally realistic range of ionic strength, pH, and metal and competing metals concentrations.

2.4.1 *Sample Collection/Isolation*

A reverse osmosis isolation technique described in Serkiz and Perdue (1990) was used to isolate a large quantity of DOM from the Suwannee River for extensive characterization of its acid-base and metal-binding properties. The Suwannee River, which drains the Okefenokee Swamp in southeastern Georgia, is a dilute freshwater stream containing relatively high concentrations of DOM (DOC values of 30-80 mg/l) and low concentrations of inorganic solutes. This unique chemical composition makes the Suwannee River an ideal site for collection of DOM. In fact, the International Humic Substances Society (IHSS) used this river as the source of their standard aquatic humic and fulvic acids, which were isolated by adsorption on XAD resins.

Samples collected by reverse osmosis (RO) were purified by cation exchange and lyophilization to produce low-ash samples that could be used to characterize proton and metal binding behavior of naturally occurring DOM.

2.4.2 Proton Binding

For reasons that will be discussed below, to describe the effect of pH on metal binding to DOM, it is first necessary to be able to describe proton binding to DOM. Proton binding data for the Suwannee River RO DOM sample from Serkiz (1991) were used in this study. These data were generated as isolated Suwannee River organic matter was titrated with strong base to determine the abundances and acidic strengths of major classes of acidic functional groups. Titrations were conducted over a range of DOM concentrations (between 50 and 5000 mg C/l) and backing electrolyte concentrations (0 and 0.5 M $NaClO_4$) to be able to describe concentration and ionic strength effects.

2.4.3 *Metal Binding*

Isolated Suwannee River organic matter was titrated with a standard $CdNO_3$ solution to examine the cadmium binding characteristics of naturally occurring DOM over an environmental realistic range of cadmium concentration, ionic strength, and pH. The effects of DOM concentration on binding of protons and metal ions was shown to be explained by simple normalization to concentration (Serkiz 1991), therefore the effects of DOM concentration were not investigated in this study. The same Suwannee River DOM sample isolated using reverse osmosis and utilized in the proton and copper binding studies described in Serkiz (1991) was also used in this cadmium binding study.

The cadmium binding study was conducted in a pH range of between 4 and 7 (held constant during the titration), and a range in backing electrolyte concentration of between 0 and 0.1 M, all at a DOM concentration of about 500 mgC/l. The experimental matrix for the cadmium binding experiments is presented in Table 2.2.

Data used to develop model fits (i.e., stability constants) were collected by potentiometric cadmium titration of a DOM solution with an ion selective electrode (ISE) to monitor free cadmium concentrations as described below. A sample of the lyophilized Suwannee River DOM was redissolved with the appropriate amount of $NaClO_4$ backing electrolyte in organic-free, carbon dioxide-free water to the desired DOM and backing electrolyte concentration. The resulting solution was then adjusted to the appropriate pH with concentrated (approximately 12 M) sodium hydroxide.

An aliquot of the DOM concentration, ionic strength, and pH adjusted solution was titrated in a Teflon titration cell, under water-saturated nitrogen gas at 25 ± 0.01 °C, with a standard $CdNO_3$ solution. The $CdNO_3$ titrant was prepared gravimetrically by dissolving a known mass of cadmium metal in a slight excess of concentrated HNO_3. The dissolved cadmium nitrate was diluted to a final concentration of about 0.1 M $CdNO_3$ in a volumetric flask. Because protons are released as cadmium is complexed by DOM, and the cadmium titrant was acidic, the pH of the DOM solution was adjusted after each incremental addition of titrant by adding 1.00 M NaOH to maintain a constant pH.

Data for the entire titration, including electrode calibration and the actual titration, were logged to an IBM XT computer. This system monitored electrode potentials of a cadmium ion specific electrode (ISE) (Orion Model 94-48) relative to a single-junction reference electrode (Orion Model 90-01) with 1.0 M $NaNO_3$ as the outer chamber filling solution. The pH of the test solution was monitored during the titration by a glass electrode (Corning Model 476022) and the same single-junction reference electrode described above and was read by an Fisher Accumet 950 pH/ion meter.

Each cadmium ion activity measurement (standard or sample) was made by monitoring the cadmium ISE at one second intervals until either 30 successive voltage reading were within a standard deviation of 0.05 mV or a total of 300 voltage readings had been made

without the convergence criterion being met, and the average potential measurement was automatically logged to the computer. After reading the potential of the cadmium ISE, the electrode potential of glass electrode was read to the nearest 0.1 mV and logged to the computer.

Prior to each titration, the cadmium ISE was calibrated with solutions of known cadmium concentration (10^{-7}, 10^{-6}, 10^{-5}, 10^{-4}, and 10^{-3} M total cadmium at a pH of 4.0) made with the same added backing electrolyte concentration as the DOM solution to be titrated. All cadmium standards were prepared in solutions of organic-free, carbon dioxide-free water. The cadmium ISE was conditioned daily by polishing with Orion polishing paper. The cadmium ISE was equilibrated at 25°C in a 10^{-7} M cadmium standard for one-half hour prior to the start of each titration.

After the electrode calibration procedure was completed, the initial cadmium ion activity of the DOM solution was determined. Subsequently, increments of cadmium titrant were manually added from a Gilmont 2.5-ml microburet and the volume of added titrant manually logged to the computer to the nearest 0.1 µl. The volume of titrant added was intended to result in a potential change for the cadmium ISE of about 5 mV. After addition of the cadmium titrant, the sample was stirred for 30 seconds to insure adequate mixing with the sample. The stirrer was then turned off to establish quiescent conditions in the titration cell. The potential of the glass electrode was then read and the pH of the solution adjusted to the initial sample pH by adding an appropriate amount of 1.0 M NaOH, while stirring, from a Gilmont 2.5-ml microburet. The volume of NaOH required to return the sample to its original pH and the glass electrode potential after pH adjustment were logged to the computer.

Cadmium titrations typically resulted in between 20 and 30 titration points. The titrations were terminated at free cadmium concentrations between 10^{-2} and 10^{-3} M for the pH 4.0 and 5.0 titrations, about 10^{-4} M for the pH 6.0 titrations, and approximately 10^{-6} M for the pH 7.0 titrations. At these concentrations, the cadmium hydroxide species are largely unimportant based on the solubility constants for these species published in Stumm and Morgan (1981).

Table 2-1. Cone penetrometer test sampling locations and depths.

CPT label	East Site Coordinate	North Site Coordinate	Ground Elevation (feet)	depth to water table (feet)	first vadose zone Soil Sample (feet)	second vadose zone Soil Sample (feet)	depth to first Water Sample (feet)	depth to first saturated Soil Sample (feet)	depth to second Water Sample (feet)	depth to second saturated Soil Sample (feet)
*A1	50095	75396	281	68	63	NA	73	75	88	90
A2	50041	74990	282	71	66	NA	76	78	91	93
A3	49997	74633	261	51	NA	NA	56	58	71	73
A4	50005	74227	241	34	NA	NA	39	41	54	56
A5	49899	73896	215	24	18	NA	28	30	38	40
B1	51100	75372	277	63	48	58	68	70	78	80
B2	51088	75269	276	62	47	57	67	69	77	79
B3	51072	75125	269	56	51	NA	61	63	71	73
B4	51049	74919	259	48	43	NA	53	55	73	75
B5	51016	74623	245	35	NA	NA	40	42	55	57
C1	51374	75563	279	62	24	57	67	69	82	84
C2	51403	75443	277	60	55	NA	65	67	80	82
C3	51433	75319	267	51	46	NA	56	58	71	73
C4	51492	75075	258	43	38	NA	48	50	63	65
D1	50215	75568	282	68	32	63	102	104	NA	NA
D2	50158	75486	282	68	63	NA	NA	NA	NA	NA
*D3	50095	75396	281	68	63	NA	NA	NA	NA	NA
D4	49952	75191	284	72	67	NA	NA	NA	NA	NA
D5	49786	74953	280	69	64	NA	NA	NA	NA	NA
E1	57029	71706	262	39	29	34	44	46	49	51
E2	56965	71612	259	37	27	32	42	44	47	49
E3	56880	71487	243	23	13	18	28	30	33	35
E4	56795	71242	222	4	NA	NA	9	11	14	16
F1	58688	72057	259	28	23	NA	30	32	35	37
F2	58621	71982	257	27	22	NA	29	31	34	36
F3	58480	71874	254	25	20	NA	27	29	32	34
F4	58223	71535	247	22	17	NA	27	29	32	34
F5	57862	71227	238	18	13	NA	21	23	26	28

* Intersection of transects 'A' and 'D'.

Table 2-2. Experimental matrix for cadmium binding to DOM experiments

pH	[DOM] (mg C l^{-1})	Added Backing Electrolyte (M)
4	500	0
4	500	0.05
4	500	0.10
5	500	0
5	500	0.1
6	500	0
6	500	0.1
7	500	0
7	500	0.05
7	500	0.10

Figure 2-1. Cross section of Transect A-A'

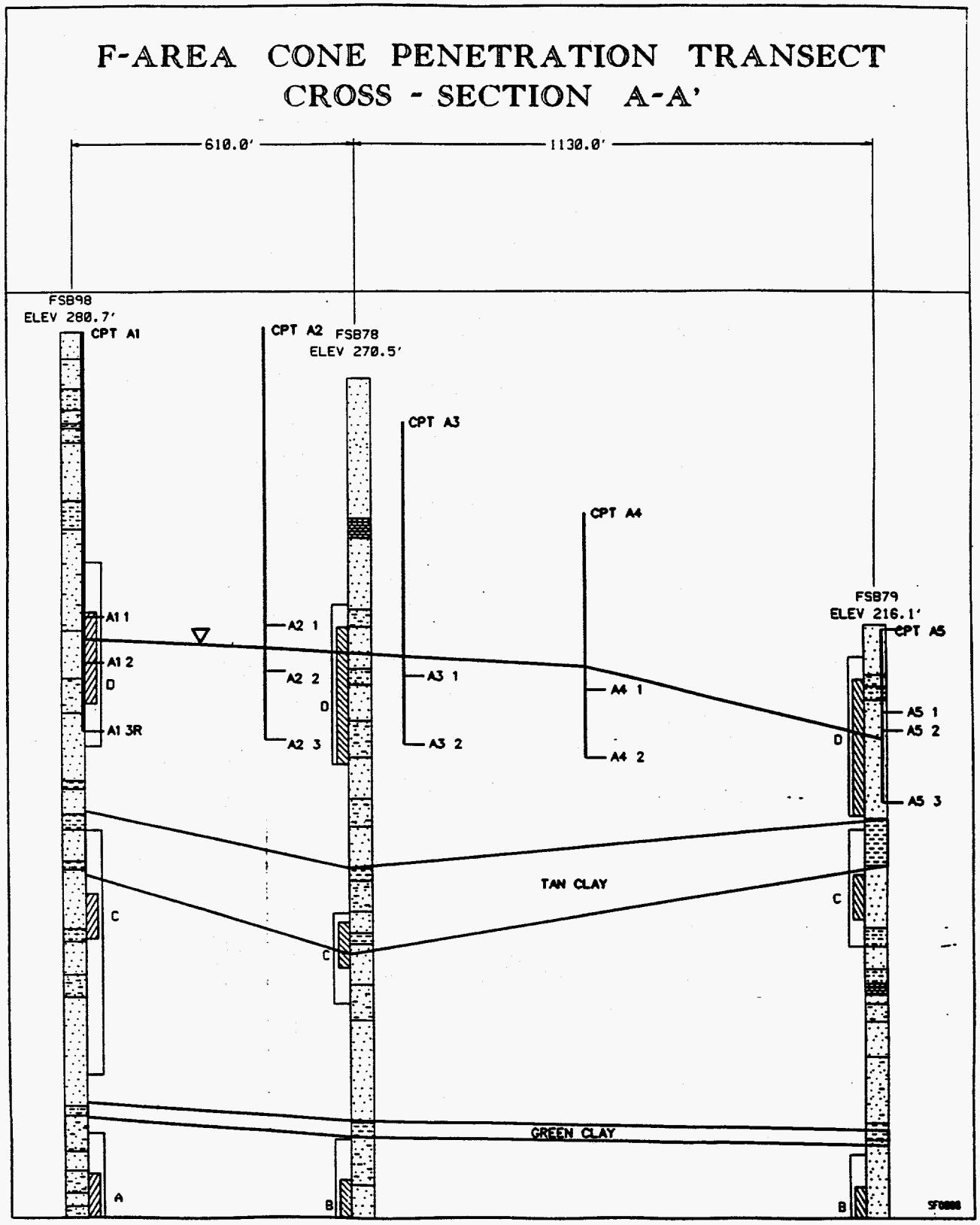


Figure 2-2. Cross section of Transect B-B'

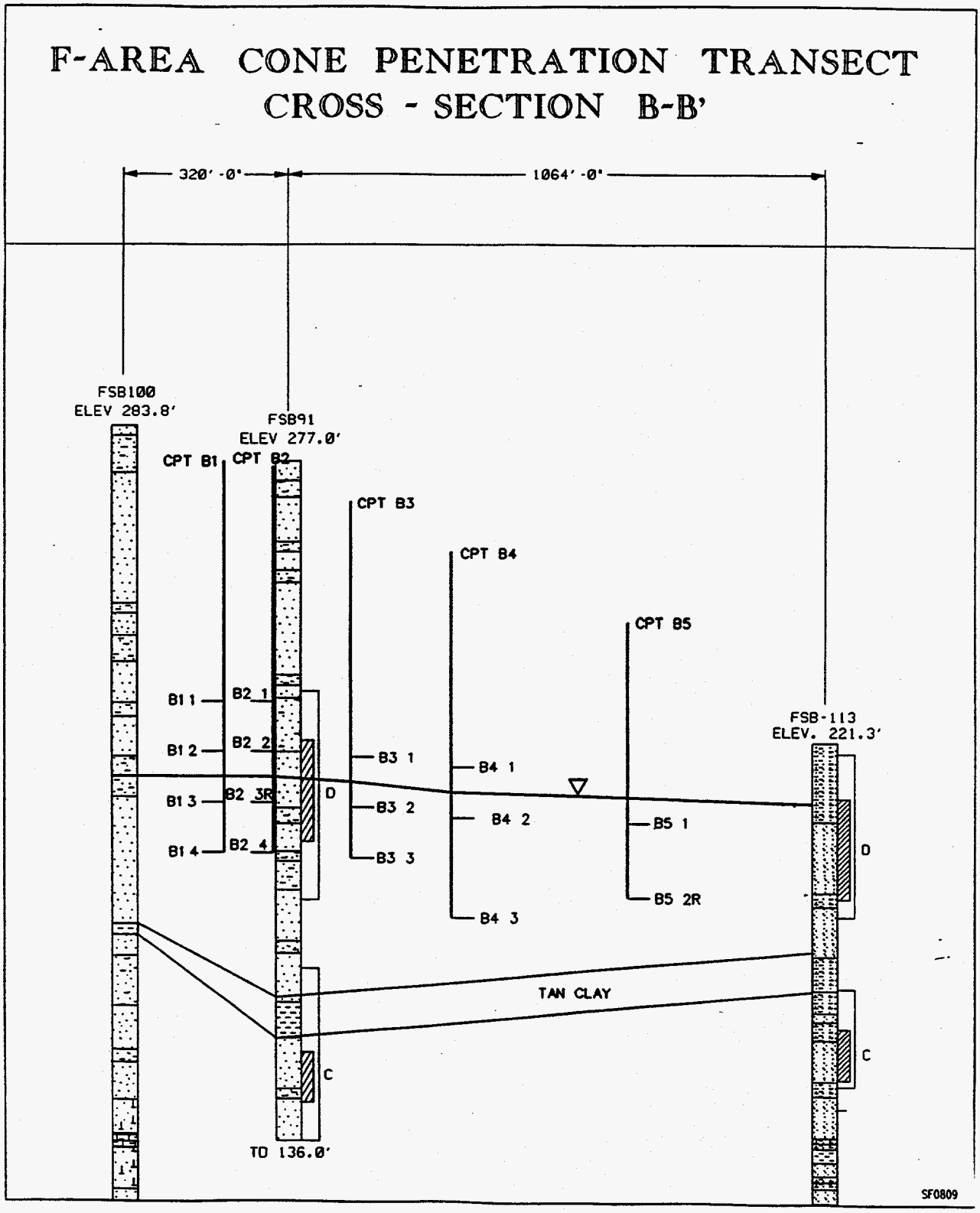


Figure 2-3. Cross section of Transect C-C'

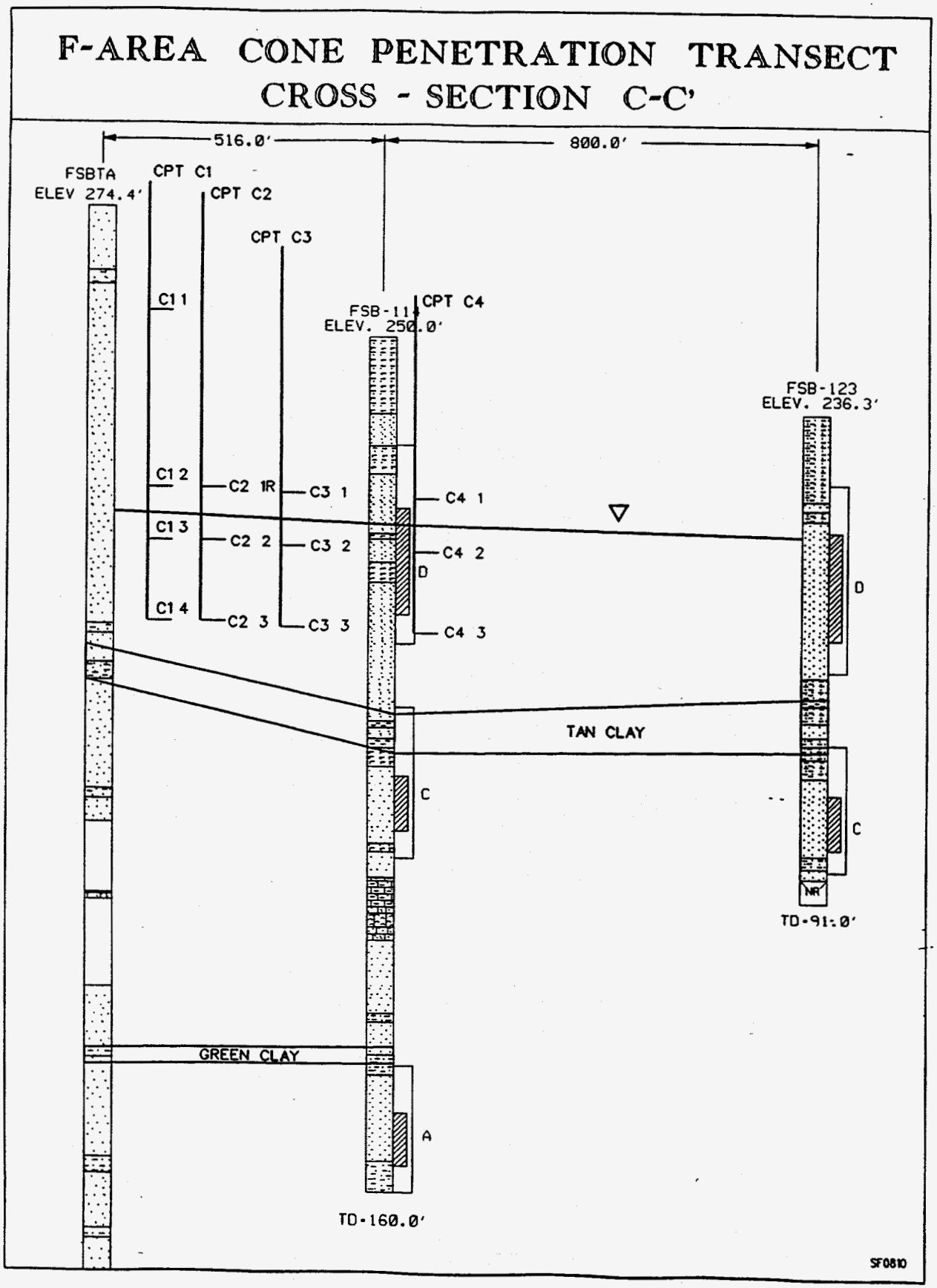


Figure 2-4. Cross section of Transect D-D'

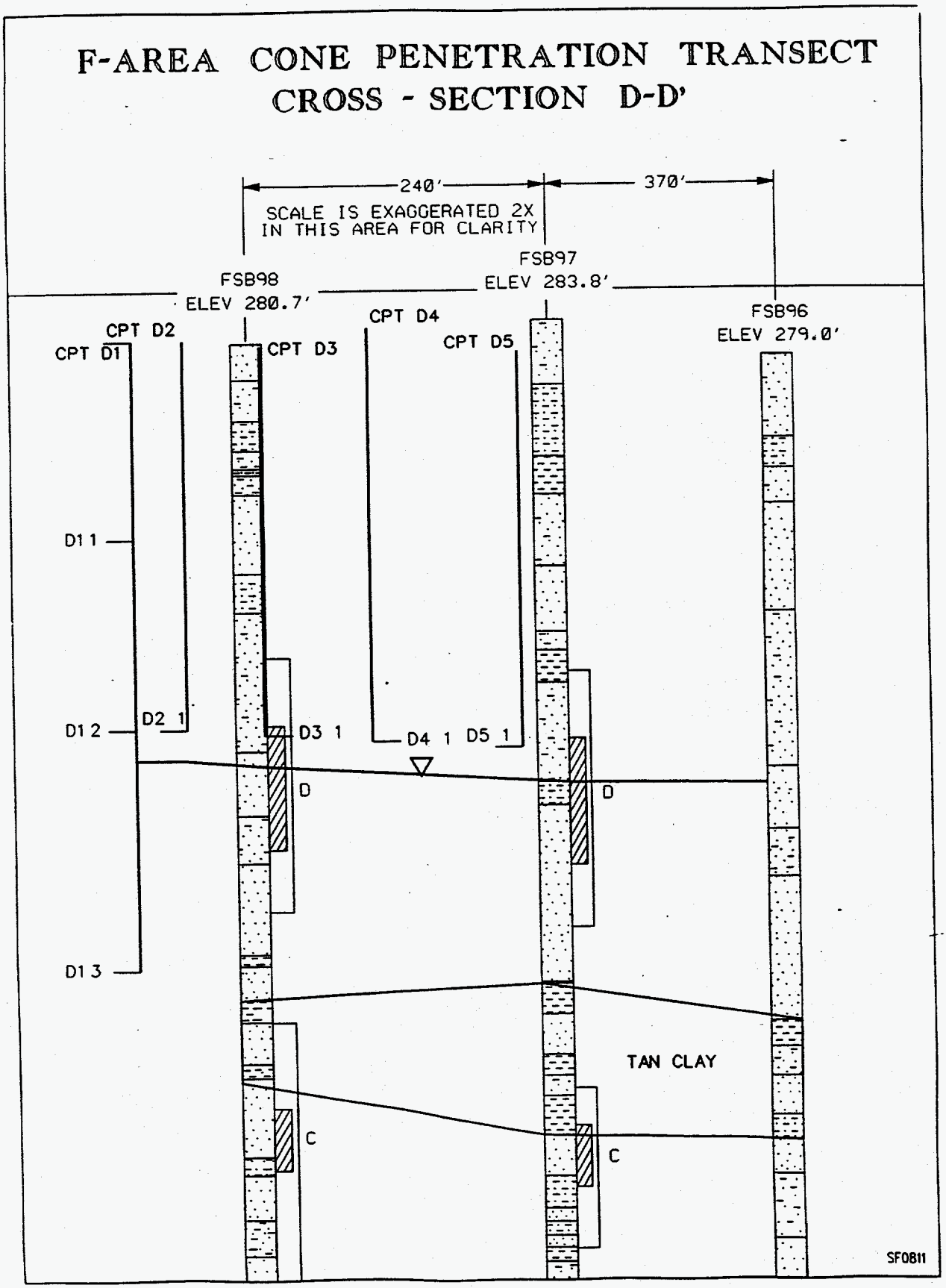


Figure 2-5. Cross section of Transect E-E'

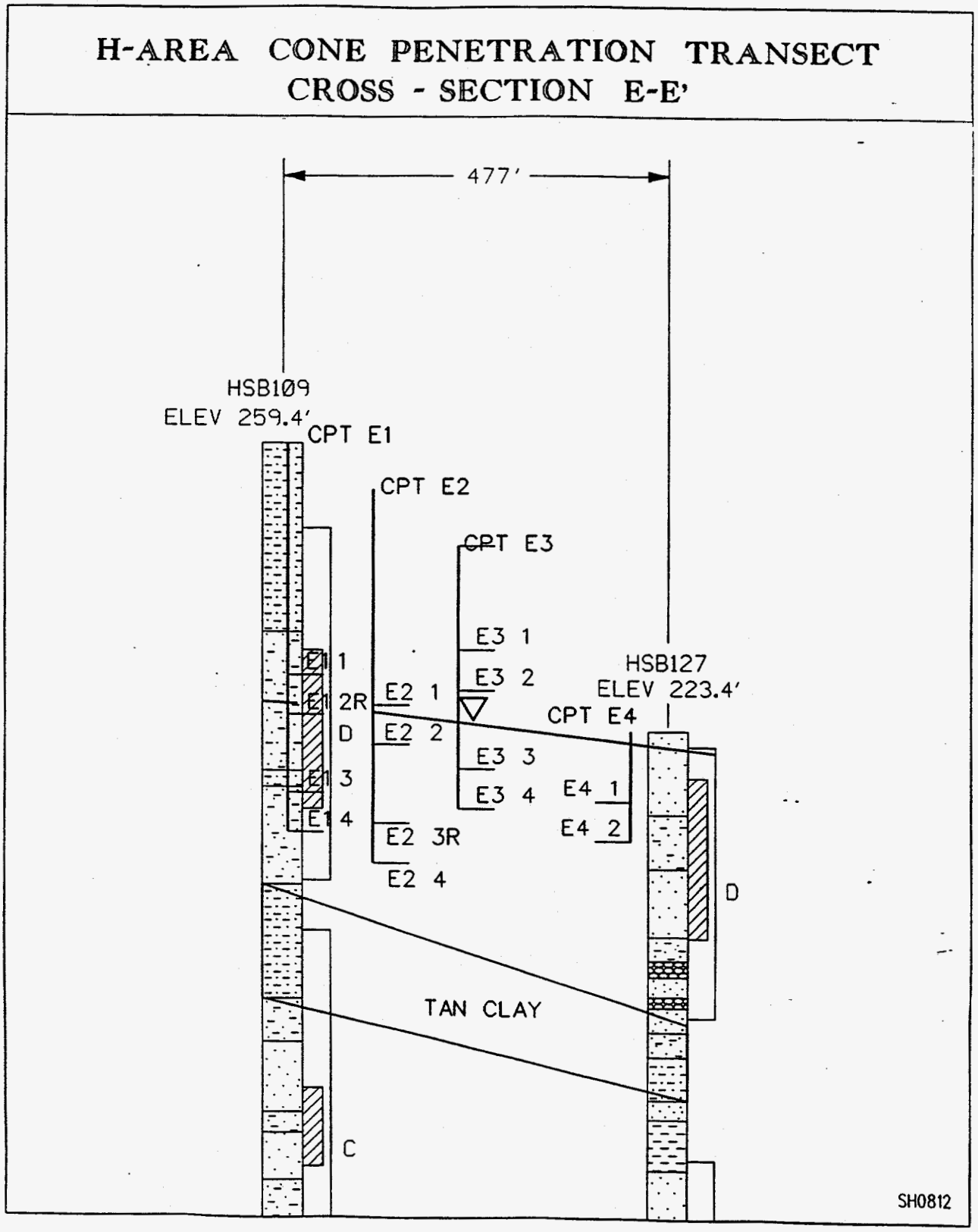
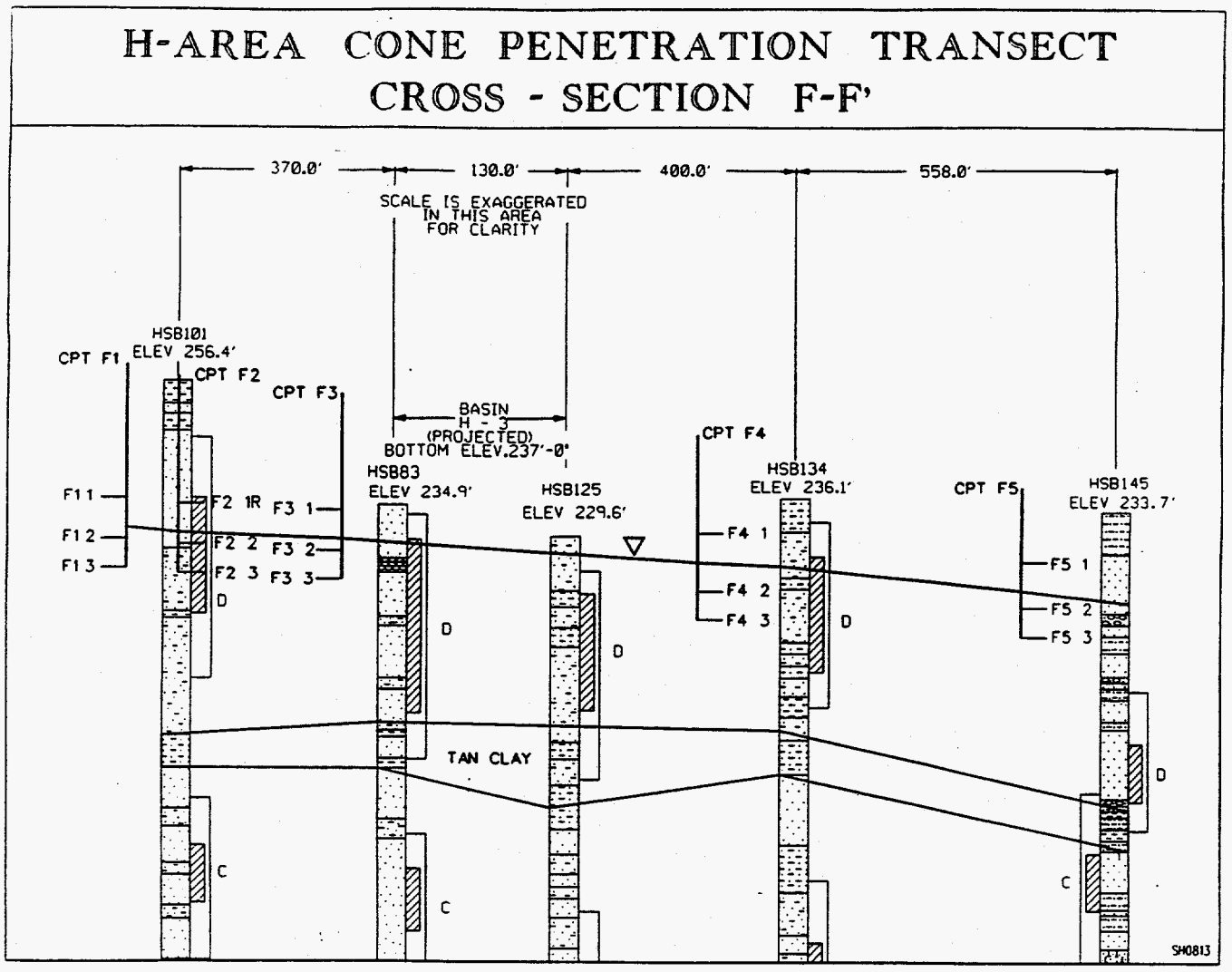


Figure 2-6. Cross section of Transect F-F'



3.0 SPECIATION MODELING BACKGROUND

The chemical form in which a molecule or ion is present in solution is referred to as its speciation . For example, cadmium can be present in a variety of species including Cd^{2+}, $CdOH^{+}$, $Cd(OH)_2^0{}_{(aq)}$, $CdCl^{-}$, and $CdNO_3^{-}$. As stated previously, the speciation of an ion or molecule affects its reactivity and, therefore its transport in the subsurface environment.

The basic idea behind surface complexation modeling is to treat the mineral or soil surface as another component, like an ion or molecule, capable of reacting with other components in solution to form a variety of species (e.g., sorbed with a metal ion, protonated or deprotonated form of the mineral surface).

Mathematical modeling using a thermodynamic equilibrium approach has been employed in this study to predict the speciation of cadmium and other metals or radionuclides. While this approach is valid for both aqueous-phase and surface-sorption speciation modeling, the empirical nature of metal/radionuclide sorption data largely necessitates that stability constants be developed on a site-by-site basis. This is due to the fact that the adsorbent phases (i.e., mineral and soil surfaces) are often a mixture of materials and their compositions and chemical characteristics vary significantly from site to site. For these reasons, aqueous-phase and surface-sorption speciation modeling have been analyzed separately in this study, although the influence of the aqueous phase on the solid phase, and visa versa has been accounted for.

The thermodynamic modeling approaches used to develop this report assume that the sorption reactions in the aquifer system are fast enough that equilibrium is achieved during groundwater transport at the basins. In reality, equilibrium conditions may not be established if the groundwater velocity is fast relative to the sorption rate. Results of kinetic sorption studies of cadmium to both background soils and individual minerals expected to be representative of surface coatings present in the aquifer show rapid equilibration in batch studies. This suggests that near equilibrium conditions should exist in the uppermost aquifer system at the FHSB.

3.1 Aqueous-Phase Speciation Modeling

MINTEQA2 (Allison et al. 1991), the U. S. Environmental Protection Agency's geochemical equilibrium speciation model, was used to estimate the speciation of cadmium present at the site. MINTEQA2 considers the total concentrations or activities of up to 50 different components, the total ionic strength, pH, redox potential and temperature of each aqueous sample to thermodynamically calculate the species present.

Input for the model includes the total component concentrations and laboratory-derived stability constants (note: stability constants present in the model database were used without modification). The MINTEQA2 model uses these inputs and the simultaneous solution of the nonlinear mass action and linear mass balance relationships to determine the equilibrium speciation for a system of a large number of competing chemical reactions.

For the simplified aqueous system containing only Cd^{2+}, $CdOH^{+}$, and $Cd(OH)_2{}^0{}_{(aq)}$, the following are the mass action and mass balance equations involved that require simultaneous solution:

Chemical Reaction

(a) $Cd^{2+} + OH^- \leftrightarrow CdOH^+$ [3-1.a]

(b) $CdOH^+ + OH^- \leftrightarrow Cd(OH)_2{}^0{}_{(s)}$ [3-1.b]

(c) $H_2O \leftrightarrow H^+ + OH^-$ [3-1.c]

Mass Action

$$K_a = \frac{\{CdOH^+\}}{\{Cd^{2+}\}\{OH^-\}} \quad [3\text{-}2.a]$$

$$K_b = \frac{1}{\{CdOH^+\}\{OH^-\}} \quad [3\text{-}2.b]$$

$$K_c = \frac{1}{\{H^+\}\{OH^-\}} \quad [3\text{-}2.c]$$

Mass Balance

$$Cd_{Total} = [Cd^{2+}] + [CdOH^+] + [Cd(OH)^0_{2(s)}] \quad [3\text{-}3]$$

The {}'s in the above equations represent the activity of each of the species. Activity can be related to concentration (represented by [ ]) by activity coefficients (γ) with the following equation:

$$\{\ \} = [\ ]\gamma \quad [3\text{-}4]$$

Activity coefficients correct for nonideality of solutions that arise from electrostatic interactions that occur with increasing ionic strength. For simplicity, in the remainder of this section, concentration (i.e., [ ]) will be used in place of activity (i.e., { }). The actual models employed in this study, however, solve these equations in terms of activity and the activity coefficients are calculated based on solution ionic strength and species' properties (e.g., ion size) using classical thermodynamic approximations like the Davies and the Debye-Huckel equations. By definition, the activity of infinite solid phases and solute (i.e., water) are equal to 1.

In reality, there are many more reactions involving cadmium and components that can react with cadmium (e.g., the carbonate system, chloride and nitrate). In this type of approach, all the mass action and mass balance must be solved simultaneously. Computer codes, like MINTEQA2, provide a convenient way to solve these complicated systems of competing chemical reactions.

3.2 Surface Sorption Modeling

The binding of a contaminant at the solid water interface can be represented by the following chemical reaction:

$$\equiv (SOH_x)^{x-1} + M^z \leftrightarrow \equiv (SOH_x - M)^{(x+z-1)} \qquad [3\text{-}5]$$

where: $\equiv (SOH_x)^{(x-1)}$ represents the soil surface coating binding site which may be protonated, deprotonated or neutrally charged;
x is the number of protons associated with a binding site on the soil surface;
M is a metal ion in with charge z; and
$\equiv (SOH_x\text{-}M)$ is a binding site, with a sorbed metal ion.

Because the reaction is assumed to be reversible, the equilibrium existing between the metal ion in solution and the metal ion sorbed may be described by an equilibrium constant, K, which is given by the equation:

$$K = \frac{\{\equiv (SOH_x - M)^{(x+z-1)}\}}{\{\equiv (SOH_x)^{(x-1)}\}\{M^z\}} \qquad [3\text{-}6]$$

It is often assumed that an equilibrium exists between a contaminant in the aqueous phase and that sorbed on a soil surface. This equilibrium is described by a sorption isotherm which has the general form:

$$[M_{sorbed}] = f([M_{aqueous}]) \qquad [3\text{-}7.a]$$

or

$$[\equiv (SOH_x - M^{(x+z-1)})] = f([M^z]) \qquad [3\text{-}7.b]$$

where $[M_{sorbed}]$ and $[M_{aqueous}]$ are the contaminant concentrations associated with the sorbed and aqueous phase. Some factors influencing contaminant partitioning include: the soil type (e.g., mineral surfaces present); soil binding site concentration; presence of particulate matter and colloids; contaminant concentration; competing ion concentration; and the aqueous-phase speciation of the contaminant.

Model fitting parameters generated from empirical models are generally valid only for the experimental conditions under which they were determined and, therefore, are defined as conditional stability constants. Examples of these more empirical models include the single K_d, Langmiur Isotherm, and Freundlich Isotherm models. In contrast, surface complex models like the diffuse layer, constant capacitance, and triple layer models, attempt to account for the affects of changes in solution chemistry (e.g., pH and ionic

strength) on binding of contaminants. The utility of these more mechanistic models is that, if working properly, these models have greater predictive power over a much wider range of geochemical conditions. A review of these models is presented in a separate report (Serkiz and Johnson 1994).

3.2.1 *Single K_d Model*

In this report, only the single or linear K_d model for soil-cadmium interactions will be examined. In it, the sorbed concentration ($[M_{sorbed}]$) is linearly related to the aqueous phase concentration ($[M_{aqueous}]$) and is defined as:

$$K_d \equiv \frac{[M_{sorbed}]}{[M_{aqueous}]} = \frac{[\equiv (SOH_x - M)^{(x+z-1)}]}{[M^z]} \qquad [3\text{-}8]$$

The slope of this equation (i.e., K_d) is always positive and is referred to as the distribution coefficient with units of L kg^{-1}. This approach assumes an infinite concentration of surface binding sites ($\equiv SOH_X^{(x-1)}$) and is, therefore, valid only under conditions of low surface loading and low aqueous contaminant concentration.

3.3 Modeling DOM-Metal Interactions

Modeling the effects of DOM on acid-base chemistry (i.e., proton binding) and metal speciation is complicated by the highly complex (multiligand) mixture of organic acids that comprise DOM. In spite of these complexities, classical thermodynamic equilibrium modeling can be used as the basis for the equilibrium description of these systems. The general formation reaction between a metal ion or proton (M) and a specific organic binding site (A_i) to form a 1:1 complex can be written as (Perdue and Lytle 1983a):

$$M + A_i = MA_i \qquad [3\text{-}9.a]$$

$$K'_i = \{MA_i\}/\{M\}\{A_i\} \qquad [3\text{-}9.b]$$

where M is the aqueous metal ion or proton, A_i is the fully deprotonated organic binding site, MA_i is the 1:1 complex formed, and { } represents the activity of a particular species. Unfortunately analytical constraints make both the quantification and chemical description of A_i impossible, and the determination of the formation constant K'_i for a specific binding site is, therefore, not possible.

An alternative approach to modeling the proton and metal binding properties of naturally occurring DOM as a small number of discrete binding sites, is to model DOM as a continuum of binding sites resulting from the complex mixture nature of DOM. The affinity spectrum and Gaussian distribution models, which are examples of continuous distribution models, are described below.

Hunston and coworkers (Klotz and Hunston 1971; Hunston 1975; and Thakur et al. 1980) developed an affinity spectrum method to describe the binding of small molecules to proteins. Shuman et al. (1983) applied this model to describe the metal binding properties of naturally occurring DOM. This method assumes a continuous distribution of binding sites on the DOM molecules and that the mole fraction of binding sites in a specified interval of log K' to log K'+dlog K' can be described by a continuous function (i.e., f(log K)). The affinity spectrum method is designed to numerically estimate the function f(log K) from titration data. The mass action equation for the sum of the metal bound site can be rewritten to solve for f(log K) by the affinity method as:

$$\Sigma[MA_i] = C_L \int_{-\infty}^{+\infty} \frac{K_i'[M]}{1+K_i'[M]} f(\log K')d(\log K') \qquad [3\text{-}10]$$

The integral in eqn.[3-10] can be solved for f(log K') with experimental values of $\Sigma[MA_i]$, C_L (binding site concentration), and [M] by finite difference approximation techniques.

The affinity spectrum method has been reported by Perdue (1990) to have several drawbacks: (1) it predicts rather large normal distributions of binding sites for a mixture of simple binding sites, (2) it does not yield fitting parameters that can be used in a predictive manner, (3) it requires smoothed data sets and is sensitive to the data-smoothing algorithm, and (4) it is numerically unstable to some of the empirical parameters used to estimate f(log K).

Perdue and coworkers (Perdue and Lytle 1983b; Perdue et al. 1984) have developed a continuous distribution model, similar to the affinity spectrum method of Shuman, to describe the binding of protons and metal to naturally occurring DOM. This model, known as the Gaussian distribution model, assumes that the distribution of binding sites is known and is a normal Gaussian distribution. The probability of occurrence of an acidic or metal binding functional group is related by a normal probability curve to the Gibbs' free energy (or log K') for binding to that site. In other words, within a "class" of binding sites, those binding sites whose log K' values are similar to the mean pK are far more likely to occur than are much stronger or weaker binding sites. This is demonstrated in graphical form for proton binding (H-DOM) and metal binding (M-DOM) in Figure 3-1.

The detailed mathematics of the Gaussian distribution model has been discussed by Parrish and Perdue (1989). The continuous function of f(log K') is given by:

$$f(\log K') = (\delta\sqrt{2\pi})^{-1} \exp(-0.5((\mu - \log K')/\delta)^2) \qquad [3\text{-}11]$$

Substitution into eqn. [3-10] yields:

$$\Sigma[MA_i] = \frac{C_L}{(\delta\sqrt{2\pi})}\int_{-\infty}^{+\infty}\frac{K_i'[M]}{1+K_i'[M]}\exp(-0.5((\mu-\log K')/\delta)^2)d(\log K') \qquad [3\text{-}12]$$

Model fitting parameters, μ (the most probable pK'), σ (one-standard deviation from μ for a normal distribution), and the total site concentration (C) for each class of sites were obtained by fitting the Gaussian distribution model to titration data using nonlinear regression methods for each class of binding sites.

This research includes an attempt to explain the effects of ionic strength and pH on cadmium binding to naturally occurring DOM. The Gaussian distribution equation (i.e., Equation 3-12) can be expressed in terms of thermodynamic stability constants to include ionic strength effects as:

$$\Sigma[MA_i] = \frac{C_L}{(\delta\sqrt{2\pi})}\int_{-\infty}^{+\infty}\frac{K_i'[M]\Gamma^{-1}}{1+K_i'[M]\Gamma^{-1}}\exp(-0.5((\mu-\log K')/\delta)^2)d(\log K') \qquad [3\text{-}13]$$

The stability constants obtained from eqn. [3-13] are still conditional stability constants. These stability constants, however, are conditional only on the pH at which the metal binding study was conducted and not on the ionic strength of the solution.

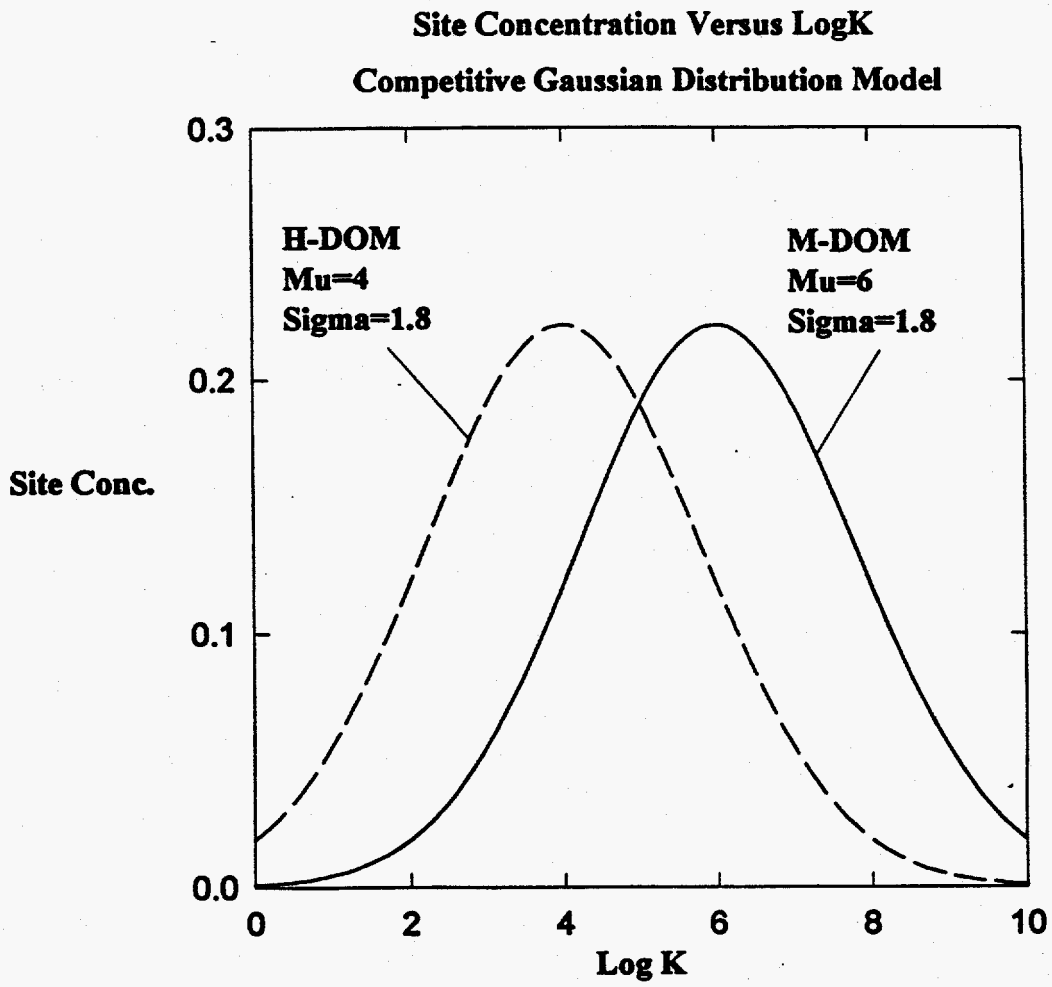
Recently, Carreira and coworkers have extended the Gaussian distribution model to a model that describes the competitive binding of proton and metal ions to DOM (Dobbs et. al. 1989a;1989b). This model allows the description of the pH dependence of metal binding and the competitive binding of several metal ions. As stated previously, the Gaussian distribution model can explain the proton binding sites of a class of sites with three fitting parameters (μ_H, σ_H, C_H (i.e., C_L for proton binding)). The competitive Gaussian distribution model assumes that the total number of binding sites is equal for protons and all metals (i.e., $C_L = C_H = C_M$) and that the shape of the distribution is the same for protons and all metals (i.e., $\sigma_H = \sigma_M = \sigma$). The model, therefore, assumes that C_L and σ are characteristic properties of a class of binding sites in the DOM and that the relative affinity of cations to binding sites is contained in the μ term for proton or metal binding.

Because C_L and σ are assumed to be independent of the nature of the cation being bound, the K ratio for the reaction of the ith ligand with a proton or metal (j) is equal for all ligands in the mixture and can be written as:

$$Q_j = \frac{10^{\mu_{Mj}}}{10^{\mu_{Hj}}} = \frac{K_{M_{ji}}}{K_{H_{ji}}} \qquad [3\text{-}14]$$

Knowing μ_{H+}, σ_{H+}, and C_{H+} (i.e., most probable log K, the shape of the Gaussian distribution, and the concentration of binding sites) for proton binding to DOM, the competitive Gaussian distribution model can be fit to data in the form of free metal versus bound metal to yield the most probable logK (μ_M) for metal binding.

Figure 3-1. Example of the distribution of log K' values for naturally occurring DOM



4.0 RESULTS

4.1 Aqueous Sample Geochemistry

Aqueous samples obtained in this study spanned a wide range of geochemical conditions. Sample pH varied from 3.1 and 7.1, while Eh values were between +41 and +442 mV. Samples typically had high nitrate and ^3H concentrations. Nitrate levels varied from 3.9 to 1600 mg l^{-1}. ^3H levels ranged between 180 and 1.12×10^6 Bq l^{-1}. The major cations in the samples included Al^{3+}, Fe^{3+}, K^+, Mg^{2+}, and Na^+. Although not specifically analyzed for, $HSiO_4$ is expected to be present as a major cation. The major ion chemistry is consistent with the addition of large amounts of nitric acid to the system and the dissolution of both clay minerals (e.g., kaolinite) and existing surface mineral coatings (e.g., iron (oxy)hydroxides). Typical ionic strength of the samples was approximately 1×10^{-1} mol l^{-1}. Conductivities varied widely, and were inversely correlated with pH. At low-pH values, where the effects of the contaminant plume were most obvious, conductivities were between 5 and 35 S m^{-2}. Aqueous samples with minimal impact had typical conductivities of less than 3 S m^{-2}. Aqueous inorganic carbon content was found to be < 1 mg l^{-1} in all samples.

Cadmium was observed above detection limits in 35 of 53 aqueous samples from the F- and H-Area Seepage Basins (FHSB). Concentrations were found to range from 0.48 to 23.5 μg l^{-1}, with a mean concentration of 3.1 ± 4.3 μg l^{-1}. Results are reported in Tables 4-1 to 4-7.

4.2 Soil Geochemistry

4.2.1 *Particle Size Distribution*

The size of the soil particles must be considered when trying to predict the binding of a contaminant to the soil. The number of potential contaminant binding sites on the soil is directly related to the surface area of the particles. Surface area is an inverse cubic function of the radius of the soil particles. One gram of clay particles will have as much as a million times more surface area, and potential binding sites, than the same weight of larger diameter sand particles.

Using the USDA soil classification scheme (Soil Survey Staff 1975), the subsurface soils downgradient of FHSB examined in this study are sands, loamy sands and sandy loams. A listing of the sand, silt and clay fraction of each sample is included in Tables 4-8 to 4-13. Samples from F-Area were sands and loamy sands. Sand content varied from 73 - >99%. Silt and clay contents were 0 -12 and 0.5 - 22% respectively. H-Area samples typically had a higher clay content than F-Area samples and can be generally classified as sandy

loams or loamy sands. Sand content in H-Area samples was between 57 and 94%. The silt and clay fractions of the samples was 0-10% and 2-42% respectively.

4.2.2 *Cation Exchange Capacity*

The cation exchange capacity (CEC) of a soil is a measure of the quantity of readily exchangeable cations present in the soil. CEC is generally highly correlated with the clay content of the soil and, mechanistically, is often thought of as the quantity of clay inner layer binding sites capable of undergoing exchange reactions. In reality, analytical techniques used to quantify CEC probably measure both these inner layer exchange sites as well as some weaker exchange sites associated with the outer surface of the mineral matrix. CEC can be used to estimate how easily a positively charged groundwater contaminant can replace the cations which naturally are associated with the soil surface.

The CEC of the soils analyzed in this work were relatively low. This is probably due to the high percentage of sand in the F- and H-Area soils. Sand, being of larger radius than silt or clay, has less surface area available to undergo ion exchange and contains no inner layer exchange binding sites that are present in clays. Samples with a higher fraction of clay and silt, have more surface area and inner layer exchange sites available for ion exchange, and therefore a higher CEC. The CEC for the soils examined in this study are listed in Tables 4-15 to 4-20. The CEC was found to vary from <1 - 29 meq kg^{-1}. There is a direct correlation between the clay fraction of the soil and the CEC.

4.2.3 *Cadmium*

Based on the 43 of 86 soil samples for which cadmium was above the detection limit, the concentration in the soil ranged 88.5 to 1090 μg kg^{-1} (see Tables 4-1 to 4-7). The mean soil concentration was 214±167 μg kg^{-1}. These values are consistent with a previous study on cadmium concentrations in shallow SRS soils in which a range of 120 to 1190 μg kg^{-1} and a median value of < 600 μg kg^{-1} was reported (Looney 1990). The mean of detectable concentrations in the current study is less than the concentrations observed in two upgradient samples collected from a like depth. The soil concentrations of the upgradient samples were 293±214 and 431±293 μg kg^{-1}.

In analyzing the results, one total digestion replicate of soil sample E12(R) was not included in the average. The cadmium concentration observed in this replicate was two orders of magnitude greater than the concentrations of the other two replicates (27,000 μg kg^{-1}, compared with <711 μg kg^{-1} and 300 μg kg^{-1}).

4.3 Aqueous-Phase Speciation

In natural systems, cadmium exists exclusively in a 2^+ oxidation state. Using MINTEQA2, aqueous speciation modeling was conducted for cadmium based on the geochemical conditions observed in a representative porewater sample (sample B24) and a range of pH between 2 and 7 and Eh between -200 and +500 mV. The total aqueous cadmium concentration set equal to
1×10^{-5} M. The major ion chemistry for this sample, which was used as input data for the modeling run, is listed in Table 4-21. Over this entire range of geochemical conditions, approximately 97% of aqueous cadmium is expected to be Cd^{+2}. The remaining aqueous cadmium is predicted primarily in the form of $CdNO_3^+$, $CdCl^+$, and $CdSO_4^0$ complexes. $CdOH^-$, $Cd(OH)_2^0$, and $CdCO_3^0$ aqueous complexes are not predicted to form significant concentrations until the solution pH is greater than 9. Based on MINTEQA2 calculations, the redox potential of the groundwater will have little influence on the aqueous cadmium speciation.

In general, cadmium is soluble in acids, but not in alkali solutions. Figure 4-1 is a plot of predicted cadmium speciation versus total cadmium concentration and solution pH. As the total cadmium in a system increases, the pH at which the $Cd(OH)_{2(s)}$ precipitate becomes the dominate form of cadmium decreases.

4.4 Cadmium Partitioning

4.4.1 *Field Observed Data*

K_d values for cadmium were calculated for the 18 samples with both soil and aqueous concentrations greater than the analytical detection limit. Values range from 5.4 to 580 $l\ kg^{-1}$. Figure 4-2 presents the observed cadmium K_d value as a function of aqueous sample pH.

Figure 4-3 presents the field-derived cadmium K_d values versus clay fraction in the associated soil. Figure 4-4 is a plot of field-derived cadmium K_d values versus the CEC of the associated soil sample. These physical soil properties are not well correlated with cadmium partitioning behavior. This suggests that cadmium observed in the soil is associated with non-exchangeable binding sites (as defined by the CEC analytical procedure) rather than exchangeable sites on the surface.

4.4.2 Laboratory Studies

Figure 4-5 details the results of the cadmium sorption kinetic studies conducted on an uncontaminanted upgradient soil. An initial equilibrium is obtained rather quickly (<15 minutes). After approximately 1000 minutes, the results show that the system begins to

achieve a new equilibrium. This change is most noticeable with in the experiment performed with an initial pH of 5.3. This second equilibrium may be the result of one of several phenomenon. The first possibility is that it represents a second type of surface binding site or sorption mechanism. It may also be the result of changes in soil surface area caused by the fractionating of soil particles during shaking. Finally, it may represent the precipitation of cadmium onto the soil surface or changes in the surface sorption characteristics due to mineral dissolution. Based on these kinetics results, samples were shaken 16-18 hours (overnight) in further batch studies.

The second phenomena notable in the results of the kinetics study is the increase in cadmium sorption with increasing pH. This sorption isotherm was observed in subsequent batch studies (see Figure 4-6). At acidic pH values (less than approximately 4.5), the fraction of cadmium sorbed is negative. This means that dissolution of soil is releasing cadmium at low pH values. In this study, the fraction of cadmium sorbed at a given pH was found to be not influenced by initial solution cadmium concentration. Cadmium concentrations increased by 10 - 20 $\mu g\ l^{-1}$ in most solutions with pH values less than 4. As solution pH increased above about 4.5, the fraction sorbed increased.

Preliminary results of the soil aging experiment show that cadmium is leached from the soil by the low pH simulated waste solution. 25-l composite effluent samples collected after allowing approximately 80 and 200 pore volumes of simulated waste solution (pH = 2.5) to pass through the soil column, show an increase in cadmium concentration of 2.4 and 0.3 $\mu g\ l^{-1}$ respectively. This suggests that at least a portion of the cadmium observed in the groundwater at FHSB is a result of leaching from the native soil materials.

4.5 Sorption Modeling

The single K_d was examined with respect to its ability to predict the field observed cadmium partitioning data. The K_d value was varied to provide the "best fit" of the data as determined by the method of least squares. In this method, difference between the actual soil concentration and that predicted by the model is calculated and squared for each data point. Model fitting parameters were adjusted until the sum of the errors squared (SES), calculated using all data points, was minimized. This may be described by the equation:

$$SES = \sum_i \left([Cd_{soil}]_{observed} - [Cd_{soil}]_{predicted} \right)^2 \qquad [4\text{-}1.a]$$

where: i is the number of data points; and
$[Cd_{soil}]_{observed}$ and $[Cd_{soil}]_{predicted}$ are the observed and predicted cadmium concentrations associated with the soil respectively.

Using this method, relative errors associated with large concentration data points will weight more in parameter selection than errors from small concentration data points. To

allow equal weighting to be placed on minimizing the error associated with each data point, a relative error should be used. This was implemented by normalizing the error squared by actual soil bound cadmium concentration of that data point. Hence, eqn. [4-1] becomes

$$SES_{normalized} = \sum_i \frac{\left([Cd_{soil}]_{observed} - [Cd_{soil}]_{predicted}\right)^2}{[Cd_{soil}]_{observed}} \qquad [4\text{-}1.b]$$

Previous modeling efforts at the FHSB have used a constant K_d value of 6 for cadmium. This implies that the cadmium soil source is 6 times the aqueous concentration at a given location. Using a least squares fitting routine, it was determined that a K_d value of 15 provided a "best fit" of the observed cadmium distributions. As shown in Figure 4-7, while most cadmium soil concentrations are underestimated using a K_d of 15, the soil source term associated with very high aqueous concentrations is overestimated.

4.6 Binding to Dissolved Organic Matter

Data in the form bound metal sites (μeq/mgC) versus free metal are plotted in Figures 4-8 to 4-11. These plots show the following general trends: greater bound metal concentrations as the concentration of free cadmium in solution increases, and for a given free metal concentration, more metal is bound to the DOM at higher pHs due to the reduction in competition for binding sites with hydrogen ions.

4.6.1 *Ionic Strength Effects*

The effects of ionic strength on the binding of protons to naturally occurring DOM were investigated by titrating DOM collected from the Suwannee river at 0, 0.05, and 0.1 M $NaClO_4$ concentrations as the backing electrolyte and a DOC concentration of 500 mg C l^{-1}. Unlike many previous studies which completely neglected activity effects or developed stability constants which were conditional on the solution ionic strength, the method of activity correction developed by Serkiz (1991) was used to calculate activity coefficients. This is necessary because the ISE allows a measure of the activity and this activity must be converted to concentration to solve the mass balance equation.

This work has attempted to explain the variations observed in cadmium binding to DOM as a function of ionic strength by calculating the activity coefficients of the species of interest at each point in the titration. Activity coefficients for the free metal, ΣMA_i, ΣA_i, and inorganic carbon species were calculated from the Davies Equation. Activity coefficients for all forms of the organic matter (i.e., bound, free and protonated) were calculated from the Davies equation:

$$\log\gamma = -0.509 Z_i^2 \left[\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I \right] \qquad [4\text{-}2]$$

where: Z_i is the charge on the ith ion and I is the solution ionic strength.

The contribution of the organic matter to the overall solution ionic strength was calculated assuming an average charge on the organic matter.

Figures 4-12 through 4-14 show cadmium binding titration data sets grouped by common pH values over all backing electrolyte concentrations. The ability to superimpose curves of different backing electrolyte concentration is a good measure of the effectiveness of the electrostatic equations used in this study to calculate activity coefficients, and therefore, to accurately account for the experimentally observed effects of ionic strength on cadmium binding.

4.6.2 *pH Effects*

The effects of pH on the binding of cadmium to naturally occurring DOM were investigated by titrating Suwannee River DOM at a concentration of about 500 mgC l^{-1} and pH values of 4, 5, 6, and, 7 which were held constant over the course of the titration. Figures 4-12 to 4-14 (0, 0.05, 0.1 M backing electrolyte) illustrate the effect of varying pH at a constant backing electrolyte concentration on the binding of cadmium. As was indicated previously, cadmium binding decreases as pH decreases. This is expected since competition for binding sites on the DOM by protons in solution increases as the pH decreases.

4.6.3 *Model Fitting*

The competitive Gaussian distribution model, described above, was fit to the experimental data. These experimental data were designed to generate stability constants that explained cadmium concentration, ionic strength, and pH effects. If the model is working correctly, then a single stability constant (i.e., μ_M) should be able to describe cadmium binding behavior over all cadmium concentrations, ionic strengths and pH values.

The proton binding fitting parameters generated on the Suwannee River DOM and listed in Table 4-15 in (Serkiz 1991) were used as model input parameters in the fitting to the cadmium binding data. The model was then fit for μ_M (most probable logK) to the data to evaluate the ability of the model to explain the effects of ionic strength and pH independently and in combination. The results of modeling fitting are presented in Table 4-16. Figure 4-15 shows the experimental data over all ionic strengths at a pH of 7 and the model predicted values for the same data set. The model fit is generally quite good with the model underpredicting the amount of bound cadmium at low free cadmium concentrations. The model fits are similar for the other pH values (see Figure 4-16)

except at lower pH values the experimental curve is limited to lower bound cadmium values due to experimental constraints. Overall, the model appears to be able to describe the data with a single stability constant over the range of ionic strength and pH of this study.

Previous studies have shown that the effects of DOM concentration on proton and metal binding can be very accurately explained by normalization to aqueous DOM concentration (Serkiz 1991). Data from this study were generated at high DOM concentrations because of the increased data quality associated with the greater signal-to-noise ratio under these experimental conditions (Perdue 1990). These data, however, can be applied to any DOM concentration by linear normalization to the actual DOM concentration. This approach is implicit in the stability constants generated from this study.

Cadmium binding to naturally occurring DOM increases with the ionization of the DOM (i.e., as pH values increase) as is expected. At a given pH, cadmium binding to Suwannee River DOM is significantly less than copper binding to the same DOM (Serkiz, 1991). For example, 30 times more copper is bound to the DOM than cadmium in a similar experiment at a pH of 7. This observation is consistent with the Irving-Williams series for metal binding to carboxylic acids (Stumm and Morgan, 1981). This relationship stems from a significant decrease in logK values for metals with an nd^{10} electronic configuration (e.g., cadmium(II)) compared to nd^{9} metals (e.g., copper(II)) that has been observed in other ligand systems.

Table 4-1. Cadmium soil and water concentrations and apparent distribution coefficients for A-transect samples (F-Area). Concentration units are ppb. K_d units are l kg^{-1}.

Sample ID	Soil Cadmium	Std. Dev.	Aqueous Cadmium	Std. Dev.	K_d
A11	<351		NA		NA
A12	261	217	4.94	2.58	53
A13	263	282	3.55	1.78	74
A13R	234	273	1.09	1.48	210
A21	352	211	NA		NA
A22	<308		1.44	0.24	<210
A23	<284		1.03	0.46	<280
A31	166	164	1.91	0.85	87
A32	88.5	102	1.39	0.47	63
A41	113	90.8			
A42	146	88.4	2.06	1.82	71
A51	133	111	NA		NA
A52	279	223	0.48	0.20	580
A53	583	210	<1.0		>580
A5 110'[1]			0.62	0.25	

NA - Vadose zone samples; no associated porewater sample or K_d.
[1]Sample A5 110' was an aqueous sample only.

Table 4-2. Cadmium soil and water concentrations and apparent distribution coefficients for B-transect samples (F-Area). Concentration units are ppb. K_d units are l kg^{-1}.

Sample ID	Soil Cadmium	Std. Dev.	Aqueous Cadmium	Std. Dev.	K_d
B11	<272		NA		NA
B12	<224		NA		NA
B13	<319		12.2	1.02	<26
B14	<349		5.86	1.39	<59
B21	<211		NA		NA
B22	307	238	NA		NA
B23	<309		7.61	1.62	<41
B23R	180	291	6.06	4.35	30
B24	<283		5.26	1.62	<54
B31	<292		NA		NA
B32	137	149	1.71	0.92	80
B33	<240		0.72	0.55	<330
B41	389	39.4	NA		NA
B42	<270		1.44	0.46	<190
B43	<247		1.19	0.26	<210
B4 145'[1]			<1.5		
B51	<375		4.75	1.18	>79
B52	210	292	2.00	0.84	110
B52R	<356		1.24	0.78	<290

NA - Vadose zone samples; no associated porewater sample or K_d.
[1]Sample B4 145' was an aqueous sample only.

Table 4-3. Cadmium soil and water concentrations and apparent distribution coefficients for C-transect samples (F-Area). Concentration units are ppb. K_d units are l kg^{-1}.

Sample ID	Soil Cadmium	Std. Dev.	Aqueous Cadmium	Std. Dev.	K_d
C11	<215		NA		NA
C12	132	124	NA		NA
C13	126	167	23.5	4.59	5.4
C14	141	122	3.19	0.93	44
C21	<163		NA		NA
C21R	196	135	NA		NA
C22	170	199	<1.5		>110
C23	<286		1.81	0.91	<160
C31	<248		NA		NA
C32	129	21.8	<1.0		>130
C33	<153		<1.0		
C41	<127		NA		NA
C42	213	368	<1.0		>213
C43	<267		<1.0		

NA - Vadose zone samples; no associated porewater sample or K_d.

Table 4-4. Cadmium soil and water concentrations and apparent distribution coefficients for D-transect samples (F-Area). Concentration units are ppb. K_d units are l kg^{-1}.

Sample ID	Soil Cadmium	Std. Dev.	Aqueous Cadmium	Std. Dev.	K_d
D11	<139		NA		NA
D12	<212		NA		NA
D13	93.8	20.2	<1.5		>63
D13RA	119	192	<1		>120
D13RB	<131		NA		NA
D21	<129		NA		NA
D41	<139		NA		NA
D51	246	92.3	NA		NA

NA - Vadose zone samples; no associated porewater sample or K_d.

Table 4-5. Cadmium soil and water concentrations and apparent distribution coefficients for E-transect samples (H-Area). Concentration units are ppb. K_d units are l kg^{-1}.

Sample ID	Soil Cadmium	Std. Dev.	Aqueous Cadmium	Std. Dev.	K_d
E11	<248		NA		NA
E12	<106		NA		NA
E12R	300	280	NA		NA
E13	132	161	0.90	1.02	150
E14	157	239	1.25	0.45	130
E21	<143		NA		NA
E22	<252		NA		NA
E23	323	319	0.99	0.52	330
E23R	296	120	2.42	0.45	120
E24	95.0	32.1	1.24	0.23	76
E31	138	107	NA		NA
E32	121	144	NA		NA
E33	<190		0.89	0.62	<210
E34	<133		1.42	0.49	<94
E41	102	119	<1.5		>68
E42	209	201	<1.5		>140

NA - Vadose zone samples; no associated porewater sample or K_d.

Table 4-6. Cadmium soil and water concentrations and apparent distribution coefficients for F-transect samples (H-Area). Concentration units are ppb. K_d units are l kg^{-1}.

Sample ID	Soil Cadmium	Std. Dev.	Aqueous Cadmium	Std. Dev.	K_d
F11	183	105	NA		NA
F12	97.5	81.1	1.00	0.26	98
F13	<419		<1.5		
F21	122	28.8	NA		NA
F21R	1086	1400	NA		NA
F22	<122		0.58	0.43	<210
F23	<227		<1.5		
F31	<323		NA		NA
F32	<256		<1.5		
F33	<224				
F41	137	90.1	NA		NA
F42	102	112	<1.5		>68
F43	<210		1.43		<150
F51	<181		NA		NA
F52	<126		<1.5		
F53	125	191	<1.5		>96

NA - Vadose zone samples; no associated porewater sample or K_d.

Table 4-7. Cadmium soil concentration data for up-gradient soil samples collected at the Little Grand Canyon (F-Area). Units are ppb.

Sample ID	Soil Cadmium	Std. Dev.	Aqueous Cadmium	Std. Dev.	K_d
GC4	293	149	NA		NA
GC5	431	206	NA		NA

NA - Vadose zone samples; no associated porewater sample or K_d.

Table 4-8. Chemical and physical properties of water and soil samples in the A-transect (F-Area).

Sample ID	*Aqueous* pH	Eh (mV)	TIC (ppm)	TOC (ppm)	*Soil* % Sand	% Silt	% Clay	CEC (meq kg^{-1})	CEC Std. Dev.
A11	NA	NA	NA	NA	88.3	2.7	9.0	9.97	0.14
A12	4.16	287	<1	3.5	99.5	0	0.5	1.11	0.16
A13	4.99	41.3	<1	13	95.0	1.6	3.3	1.82	0.20
A13R	3.42		<1	2.4	93.6	3.4	3.0	3.74	0.16
A21	NA	NA	NA	NA	89.9	5.1	5.0	5.94	0.17
A22	3.19	378	<1	14	95.7	2.8	1.5	1.39	0.16
A23	3.01	442.1	<1	8	95.3	0.2	4.5	1.40	0.17
A31	3.19	345.2	<1	14	95.6	0	4.4	7.92	0.17
A32	3.5	428.9	<1	10	89.5	7.4	3.1	<1	
A41	4.8	186.8	<1	2	92.2	2.9	4.9	4.03	0.20
A42	3.29	404.1	<1	16	91.7	3.6	4.7	2.10	0.15
A51	NA	NA	NA	NA	76.5	10.0	13.5	12.5	0.17
A52	5.42	112	<1	6.1	92.6	4.8	2.5	0.68	0.18
A53	3.72		<1	1.7	91.7	6.3	2.0	0.42	0.18

NA - Vadose zone samples have no associated porewater samples.

Table 4-9. Chemical and physical properties of water and soil samples in the B-transect (F-Area).

Sample ID	*Aqueous* pH	Eh (mV)	TIC (ppm)	TOC (ppm)	*Soil* % Sand	% Silt	% Clay	CEC (meq kg^{-1})	CEC Std. Dev.
B11	NA	NA	NA	NA	80.4	4.4	15.2	10.8	0.12
B12	NA	NA	NA	NA	89.6	4.1	6.2	11.9	0.15
B13	3.24	390.8	<1	1.8	89.6	7.6	2.8	4.71	0.15
B14	3.93	198.0	<1	2.9	93.2	3.0	3.9	3.06	0.18
B21	NA	NA	NA	NA	85.3	1.8	12.9	10.3	0.22
B22	NA	NA	NA	NA	92.3	1.2	6.4		
B23	3.86	315.3	<1	3.7	90.8	4.3	4.9		
B23R	4.02		<1	2.3	93.5	2.4	2.5	3.80	0.12
B24	3.83	315.6	<1	2.7	89.9	2.7	7.5	5.69	0.22
B31	NA	NA	NA	NA	76.7	3.9	19.4	17.3	0.17
B32	4.62	205.3	<1	3.0	92.3	1.5	6.2	2.5	0.19
B33	4.64	56.4	<1	5.1	89.2	5.3	5.5	8.42	0.198
B41	NA	NA	NA	NA	83.7	4.0	12.3	12.1	0.15
B42	4.67		<1	2.1	85.3	2.1	12.6	21.4	0.14
B43	3.66		<1	2.4	98.8	0.0	1.2	3.02	0.16
B51	4.09		<1	1.3	87.3	4.5	8.2	15.1	0.14
B52	3.61		<1	1.0					
B52R	4.69		<1	1.4	91.8	4.9	3.3	2.39	0.11

NA - Vadose zone samples have no associated porewater samples.

Table 4-10. Chemical and physical properties of water and soil samples in the C-transect (F-Area).

Sample ID	*Aqueous* pH	Eh (mV)	TIC (ppm)	TOC (ppm)	*Soil* % Sand	% Silt	% Clay	CEC (meq kg^{-1})	CEC Std. Dev.
C11	NA	NA	NA	NA	84.8	6.9	8.3	4.13	0.11
C12	NA	NA	NA	NA	80.2	5.7	14.1	13.3	0.13
C13	3.68	385.9	<1	3.7					
C14	3.75	385.8	<1	2.8	84.2	9.4	6.4		
C21	NA	NA	NA	NA	82.2	5.8	12.0	11.4	0.15
C21R	NA	NA	NA	NA	80.9	6	13.1	6.82	0.11
C22	3.96	224.9	<1	3.0				1.28	0.19
C23	4.17	280	<1	2.5	84.2	9.4	6.4	6.12	0.14
C31	NA	NA	NA	NA	93.5	1.4	5.0	5.87	0.14
C32	5.53		<1	1.7	85.7	8.8	5.5	2.54	0.12
C33	4.64		<1	2.5	85.9	8.0	6.1	8.54	0.12
C41	NA	NA	NA	NA	81.0	2.6	16.4	11.5	0.13
C42	5.27		<1	3.5	90.3	1.9	7.9	11.4	0.12
C43	4.51		<1	1.5	91.0	6.0	3.0	5.04	0.12

NA - Vadose zone samples have no associated porewater samples.

Table 4-11. Chemical and physical properties of water and soil samples in the D-transect (F-Area).

Sample ID	*Aqueous* pH	Eh (mV)	TIC (ppm)	TOC (ppm)	*Soil* % Sand	% Silt	% Clay	CEC (meq kg^{-1})	CEC Std. Dev.
D11	NA	NA	NA	NA	73.3	10.7	16	8.07	0.19
D12	NA	NA	NA	NA	83.2	6.5	10.3	4.86	0.12
D13*	6.78		<1	18.6	86.7	8	5.3	1.96	0.10
D13RA	4.14		<1	1.8					
D13RB	NA	NA	NA	NA	96.7	1.3	2.0	2.55	0.10
D21	NA	NA	NA	NA	86.1	3.2	10.7	8.96	0.14
D41	NA	NA	NA	NA	78.6	4.3	17.1	11.0	0.12
D51	NA	NA	NA	NA	86.3	3.0	10.7	12.1	0.14

* The water sample for D13 was brought to the surface using a bailer apparatus.
NA - Vadose zone samples have no associated porewater samples.

Table 4-12. Chemical and physical properties of water and soil samples in the E-transect (H-Area).

Sample ID	*Aqueous* pH	Eh (mV)	TIC (ppm)	TOC (ppm)	*Soil* % Sand	% Silt	% Clay	CEC (meq kg^{-1})	CEC Std. Dev.
E11	NA	NA	NA	NA	70.4	3.7	25.9	29.3	0.12
E12	NA	NA	NA	NA	86.4	4.4	9.2	7.42	0.09
E12R	NA	NA	NA	NA	97.9	0.0	2.1	5.05	0.10
E13	4.00	132	<1	3.0	84.6	4.9	10.5	11.4	0.08
E14	4.04	181.2	<1	2.6	94.2	1.3	4.5	8.50	0.07
E21	NA	NA	NA	NA	69.4	5.9	24.3	15.7	0.11
E22	NA	NA	NA	NA	70.8	10.1	19.1		
E23	5.85	201	<1	1.9	91.1	2.5	6.4	15.5	0.17
E23R	4.32		<1	2.4	94.4	1.7	3.9	13.3	0.11
E24	3.87	191.2	<1	2.3	87.9	4.8	7.3	13.8	0.10
E31	NA	NA	NA	NA	58.1	8.5	33.4	13.0	0.09
E32	NA	NA	NA	NA	72.6	3.2	24.2	17.3	0.11
E33	4.27	277.8	<1	1.6	90.5	3.0	6.5	11.5	0.12
E34	4.05	287.6	<1	2.8	87.2	9.1	3.7	10.5	0.12
E41	5.27	230.1	<1	1.7	66.6	1.6	31.8	20.6	0.11
E42	4.87	272.3	<1	3.7	80.2	5.3	14.5	20.6	0.17

NA - Vadose zone samples have no associated porewater samples.

Table 4-13. Chemical and physical properties of water and soil samples in the F-transect (H-Area).

Sample ID	*Aqueous* pH	Eh (mV)	TIC (ppm)	TOC (ppm)	*Soil* % Sand	% Silt	% Clay	CEC (meq kg^{-1})	CEC Std. Dev.
F11	NA	NA	NA	NA	81	5.2	13.8	14.6	0.13
F12	4.30	197.3	<1	4.6	81	3.5	15.5	16.1	0.15
F13	4.90	148.3	<1	4.2				8.51	0.17
F21	NA	NA	NA	NA	84.5	7.4	8.1	11.1	0.14
F21R	NA	NA	NA	NA	85.9	4.5	8.1	9.39	0.10
F22	4.69	224	<1	5.7	86.7	5.2	8.1	7.48	0.10
F23	6.48	255.6	<1	3.2	82.9	4.1	13	11.6	0.18
F31	NA	NA	NA	NA	61.3	5.6	33.1	14.3	0.23
F32	4.85	237	<1	3.2	82.8	2.9	14.2	15.1	0.16
F33	4.77	199.1	<1	8.5	80.7	0	18.3	13.6	0.15
F41	NA	NA	NA	NA	59.1	4.7	36.1	26.7	0.23
F42	5.20	211	<1	3.4	84.2	0	17.2	11.8	0.14
F43	4.12	176.3	<1	3.7	89.2	0	14.2		
F51	NA	NA	NA	NA	70.9	0	29.6	17.4	0.16
F52	5.91	193	<1	3.1	62.5	0	42.2	19.9	0.15
F53	5.63	221.4	<1	3.6	86.3	0	16.3	13.3	0.15

NA - Vadose zone samples have no associated porewater samples.

Table 4-14. MINTEQA2 Input Sample B24

Major Ions		Trace Metals/Radionuclides	
Component	Conc (M)	Component	Conc (M)
Na^{+1}	3.961E-03	Cr_{Tot}	1.035E-07
Mg^{+2}	8.602E-05	Ni^{+2}	2.454E-06
Al^{+3}	1.072E-03	Cu^{+2}	5.243E-04
K^{+1}	2.610E-04	Zn^{+2}	7.730E-06
Ca^{+2}	2.496E-05	H_3AsO_4	5.407E-08
Mn^{+3}	7.176E-05	SeO_4^{-2}	1.162E-07
Fe_{Tot}	7.812E-05	Sr^{+2}	3.540E-07
CO_3^{-2}	1.144E-05	Cd^{+2}	1.000E-05
H_4SiO_4	1.236E-04	Ba^{+2}	1.056E-06
NO_3^{-1}	6.156E-03	Pb^{+2}	3.801E-07
Cl-1	2.475E-04	UO_2^{+2}	2.310E-06
SO_4^{-2}	4.271E-05		

Table 4-15 Gaussian Distribution proton to DOM binding parameters

c_1	μ_1	σ_1	c_2	μ_2	σ_2
8.56 meq/ g C	4.34	1.61	6.72 meq/g C	10.79	2.50

Table 4-16 Cadmium to DOM binding parameters

Added electrolyte			**pH**				
0 M	0.05 M	0.1 M	pH 4	pH 5	pH 6	pH 7	**All Data**
2.21	2.32	2.33	2.25	2.34	2.25	2.20	2.27

Figure 4-1. $Cd(OH)_2$ solubility and speciation as a function of pH and concentration

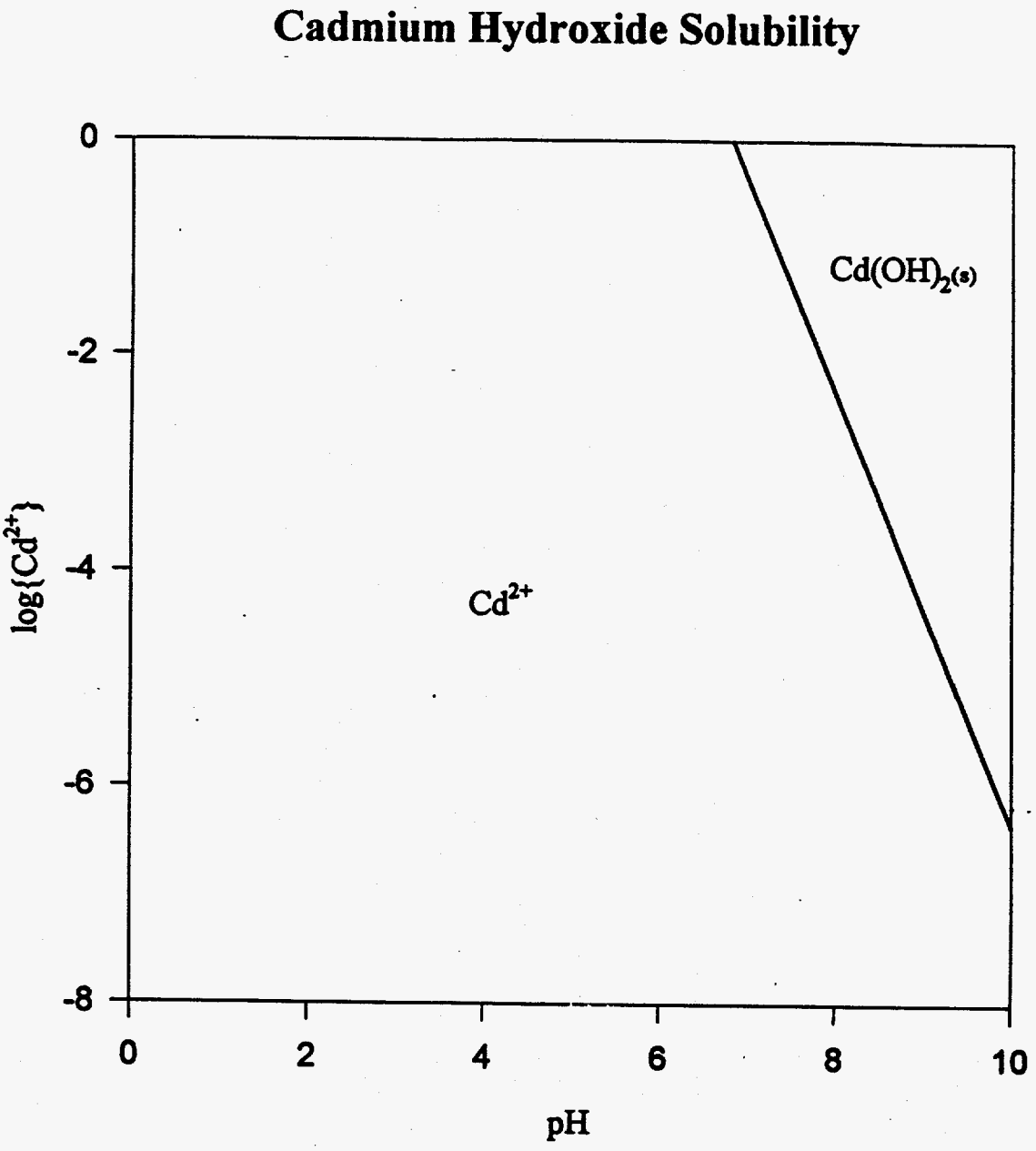


Figure 4-2. Cadmium partitioning in field samples as a function of aqueous pH

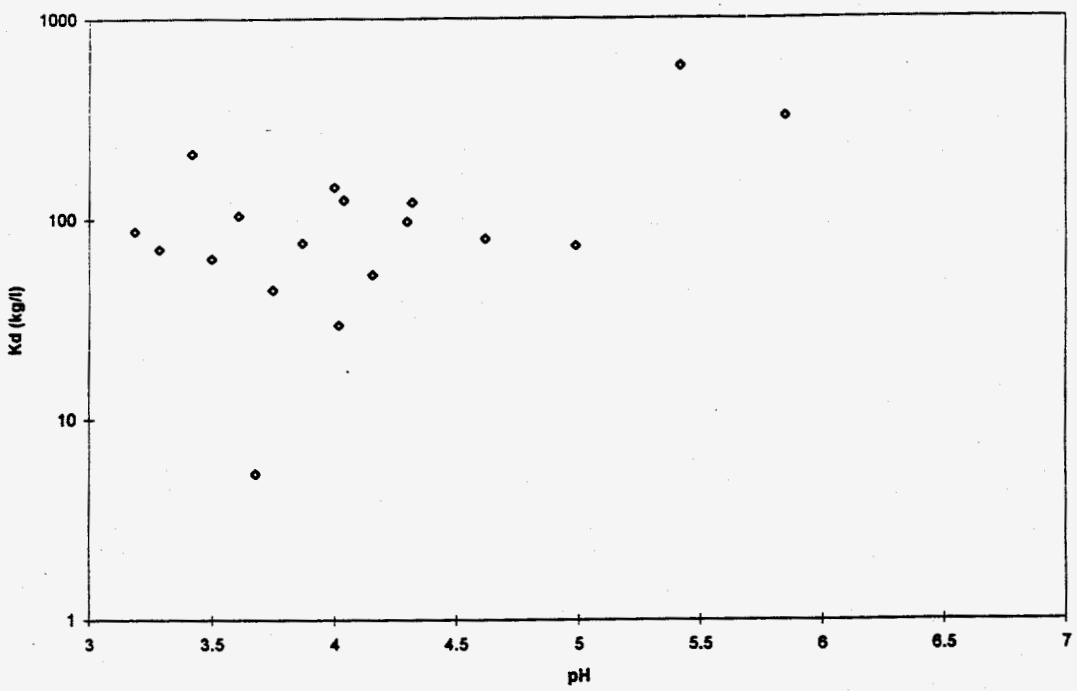


Figure 4-3. Cadmium partitioning in field samples as a function of soil clay fraction

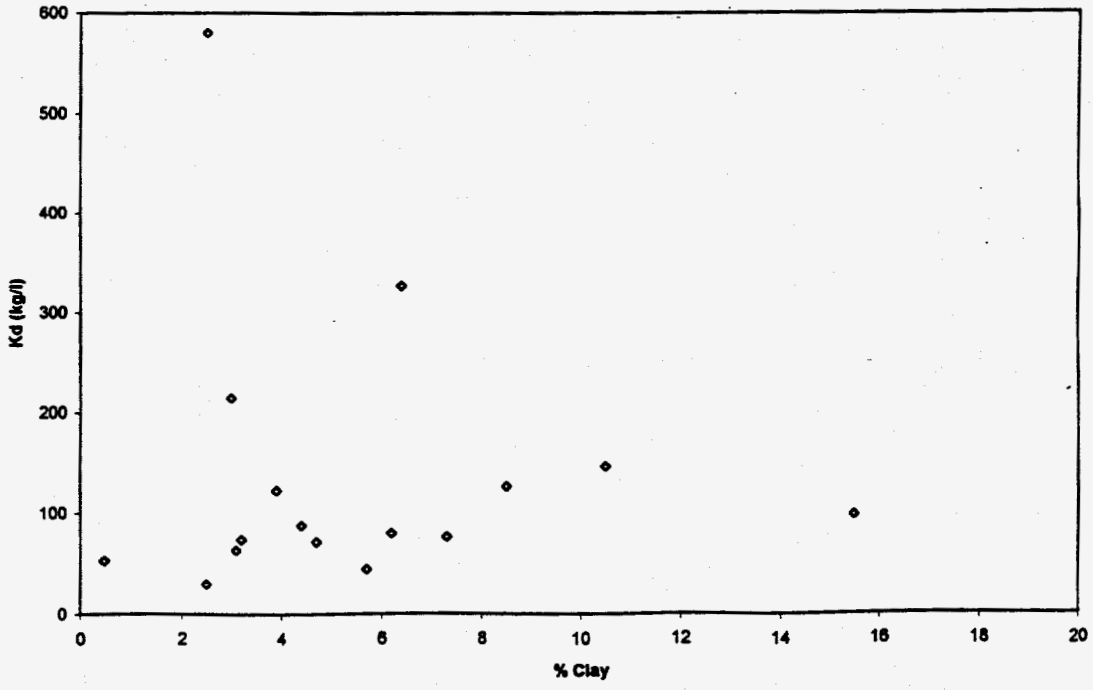


Figure 4-4. Cadmium partitioning in field samples as a function of soil CEC

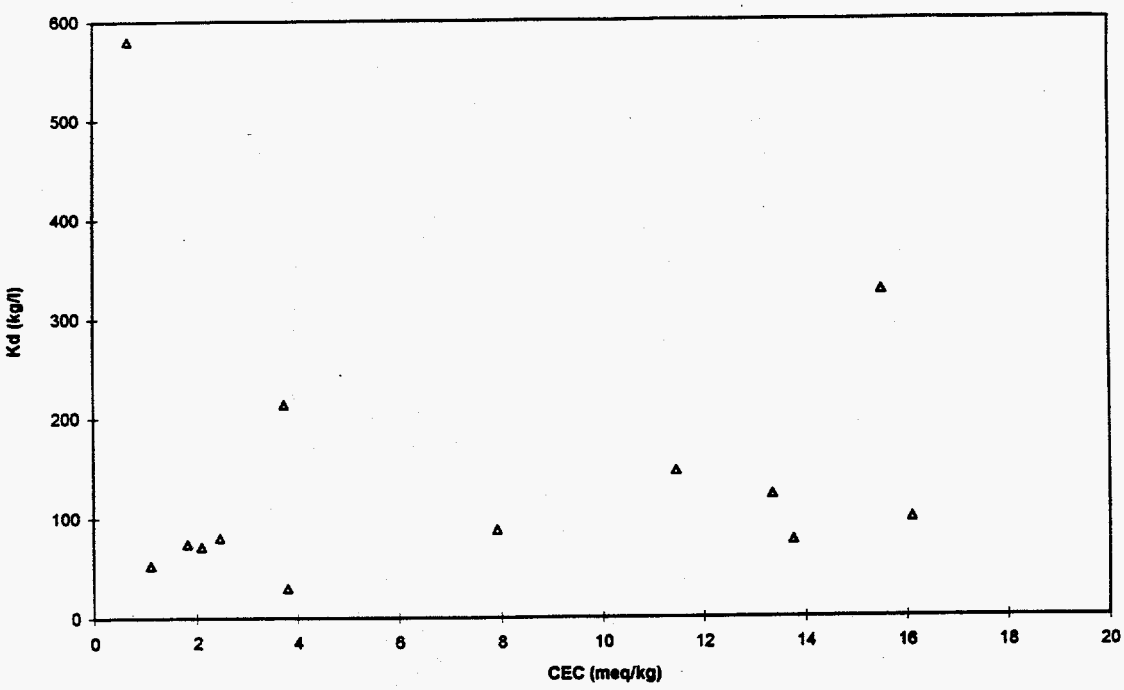


Figure 4-5. Kinetics of cadmium equilibration observed in laboratory studies

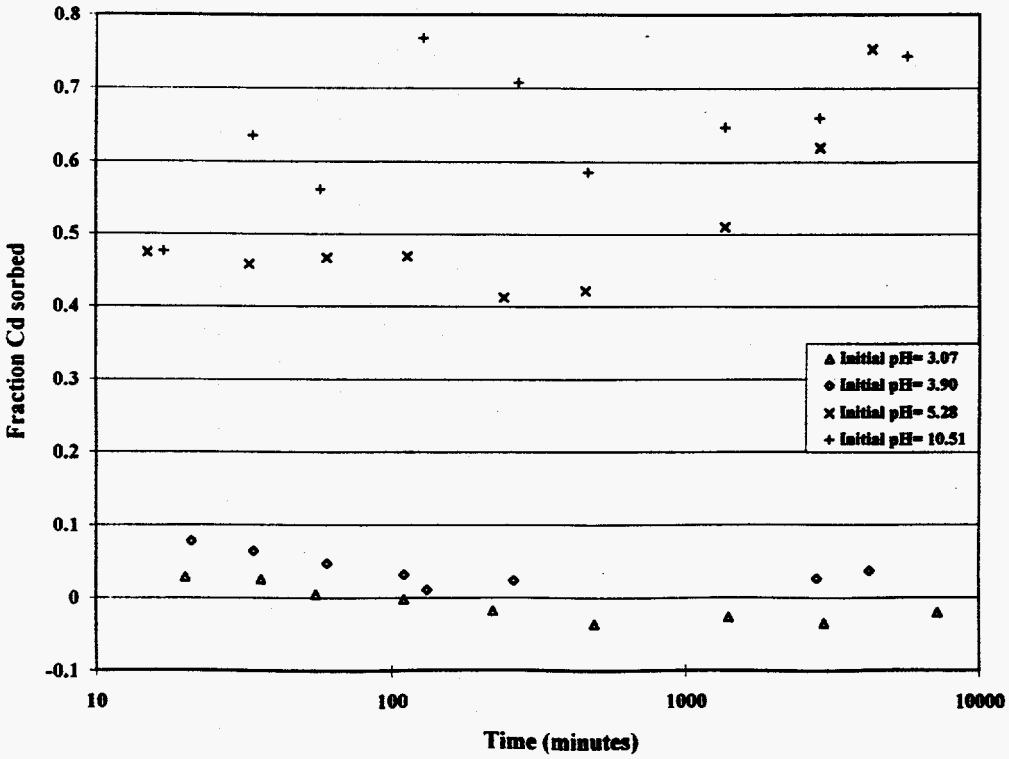


Figure 4-6. Cadmium sorption isotherms as a function of equilibrium solution pH

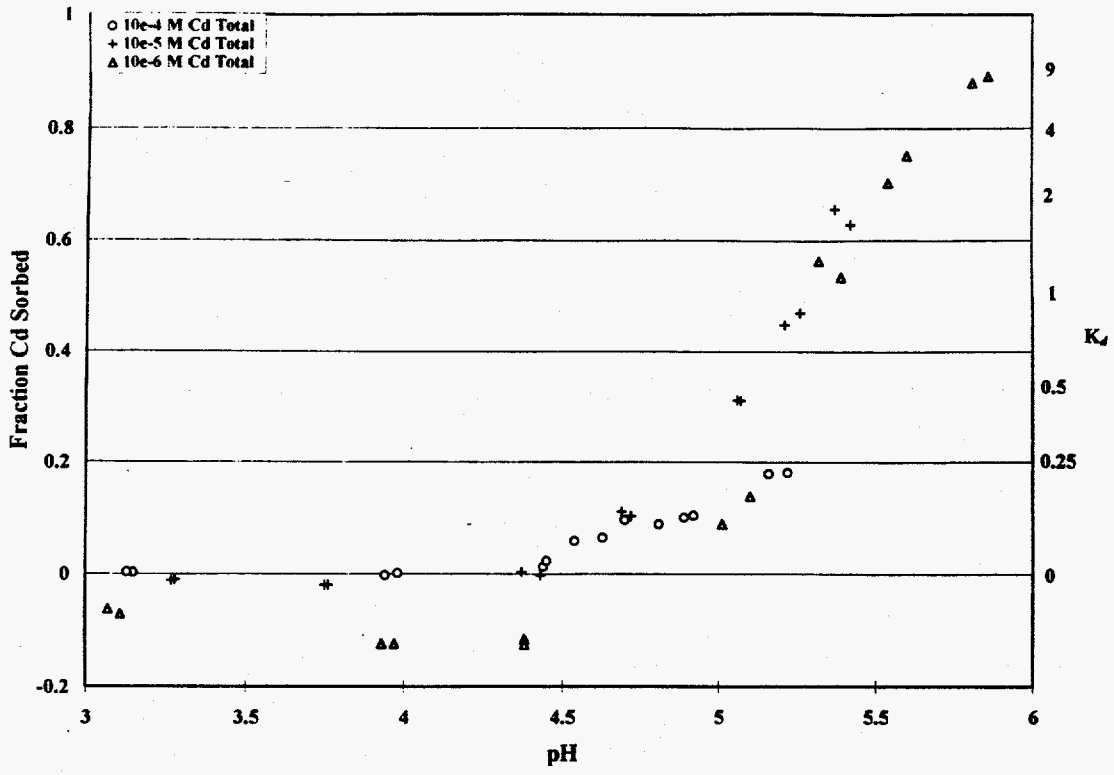


Figure 4-7. Single Kd models of field-observed cadmium soil concentration data

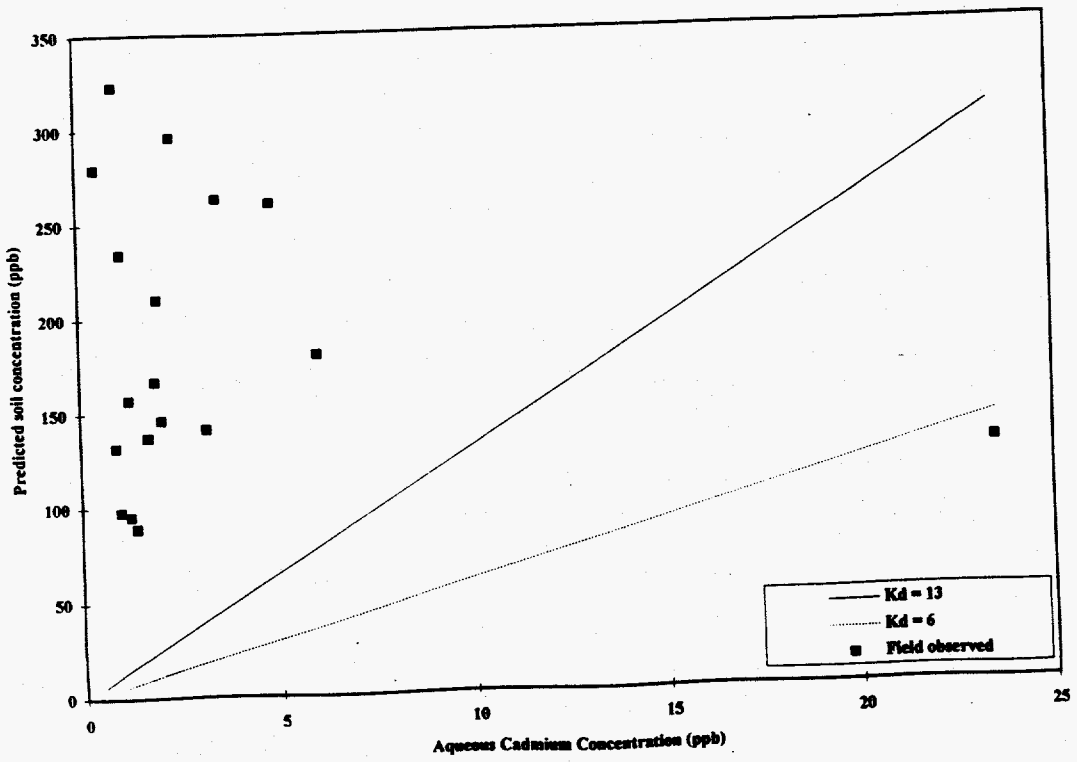


Figure 4-8. DOM bound cadmium as a function of free cadmium at pH 4 over all experimental ionic strengths

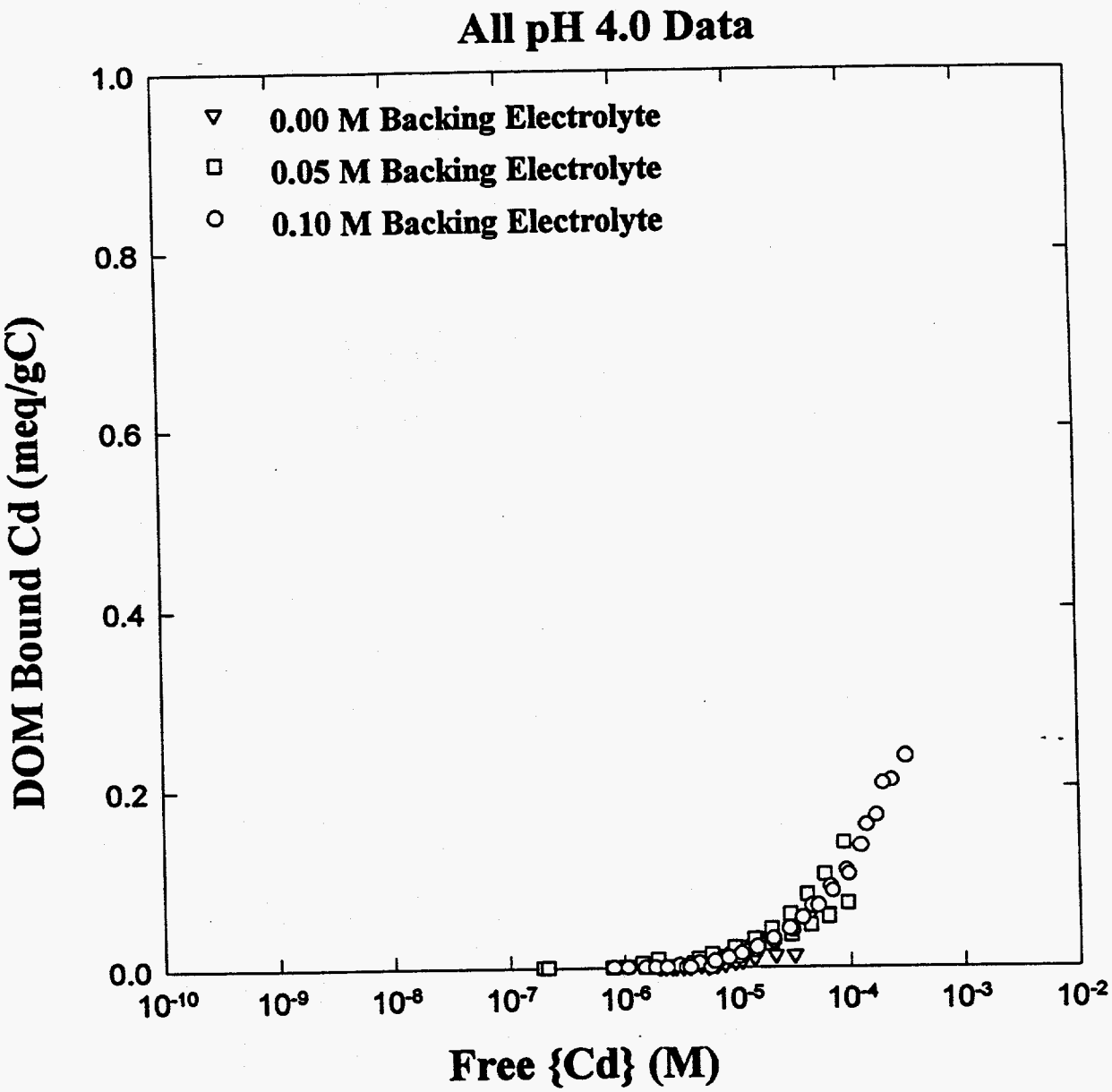


Figure 4-9. DOM bound cadmium as a function of free cadmium at pH 5 over all experimental ionic strengths

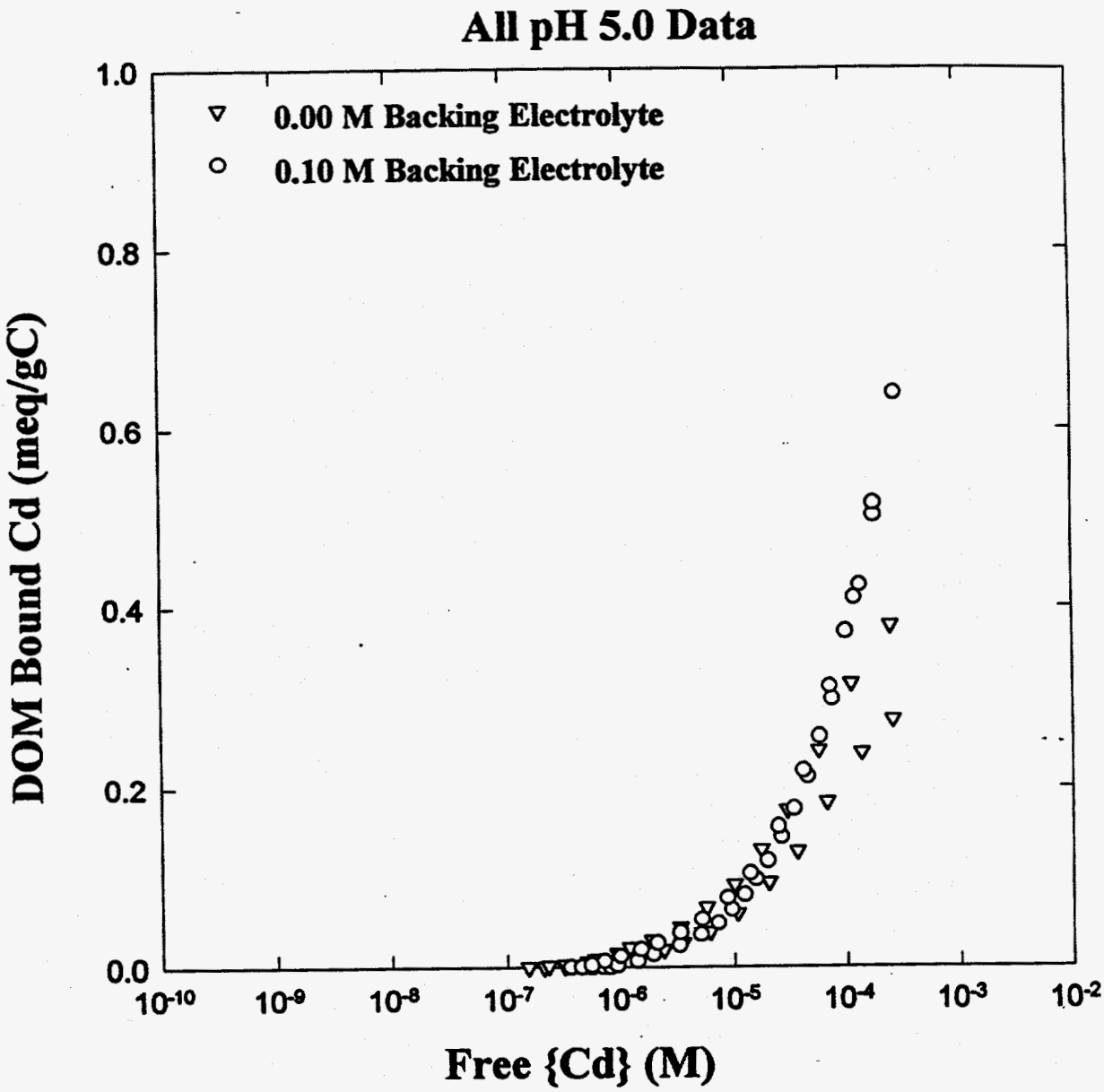


Figure 4-10. DOM bound cadmium as a function of free cadmium at pH 6 over all experimental ionic strengths

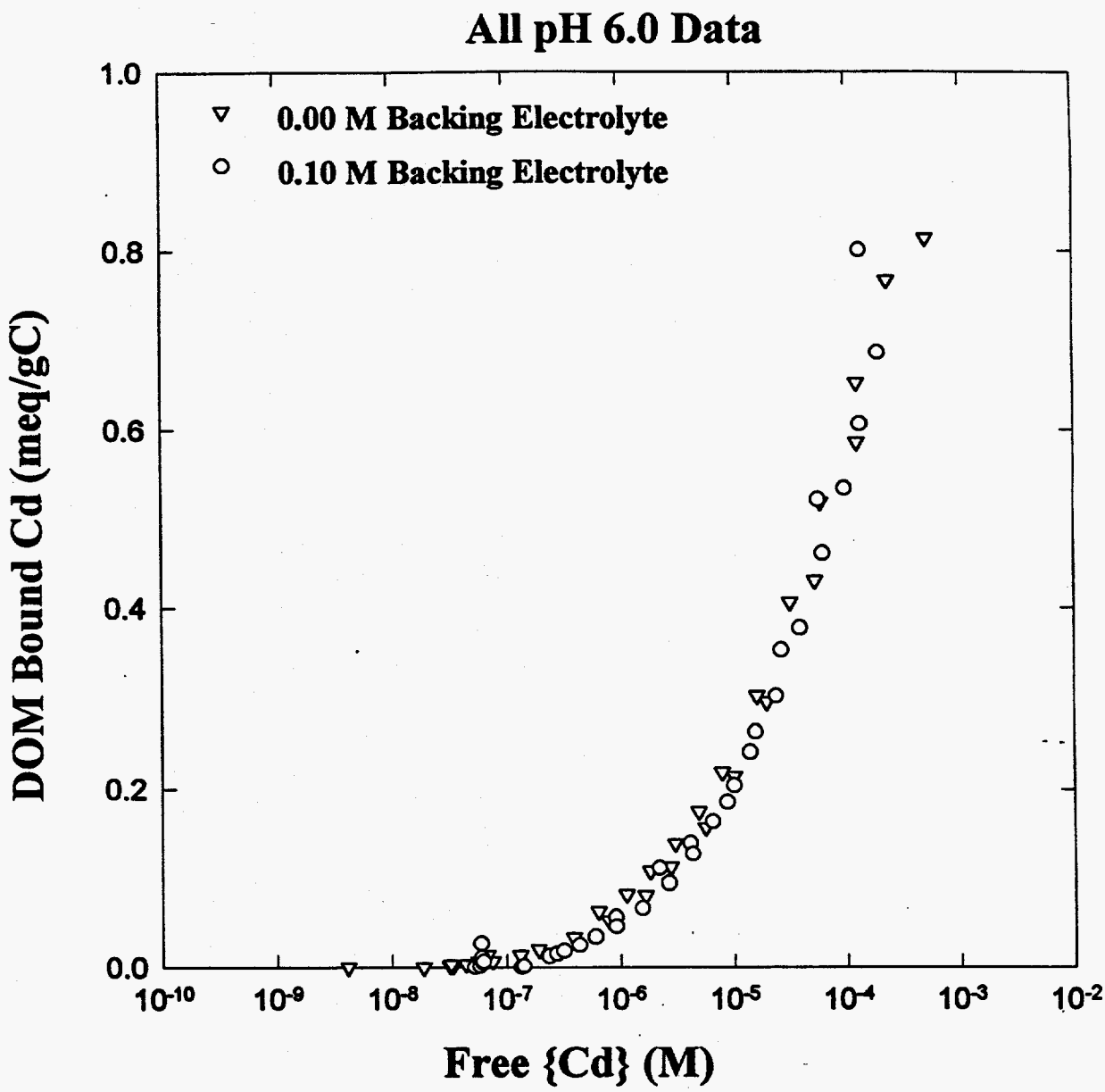


Figure 4-11. DOM bound cadmium as a function of free cadmium at pH 7 over all experimental ionic strengths

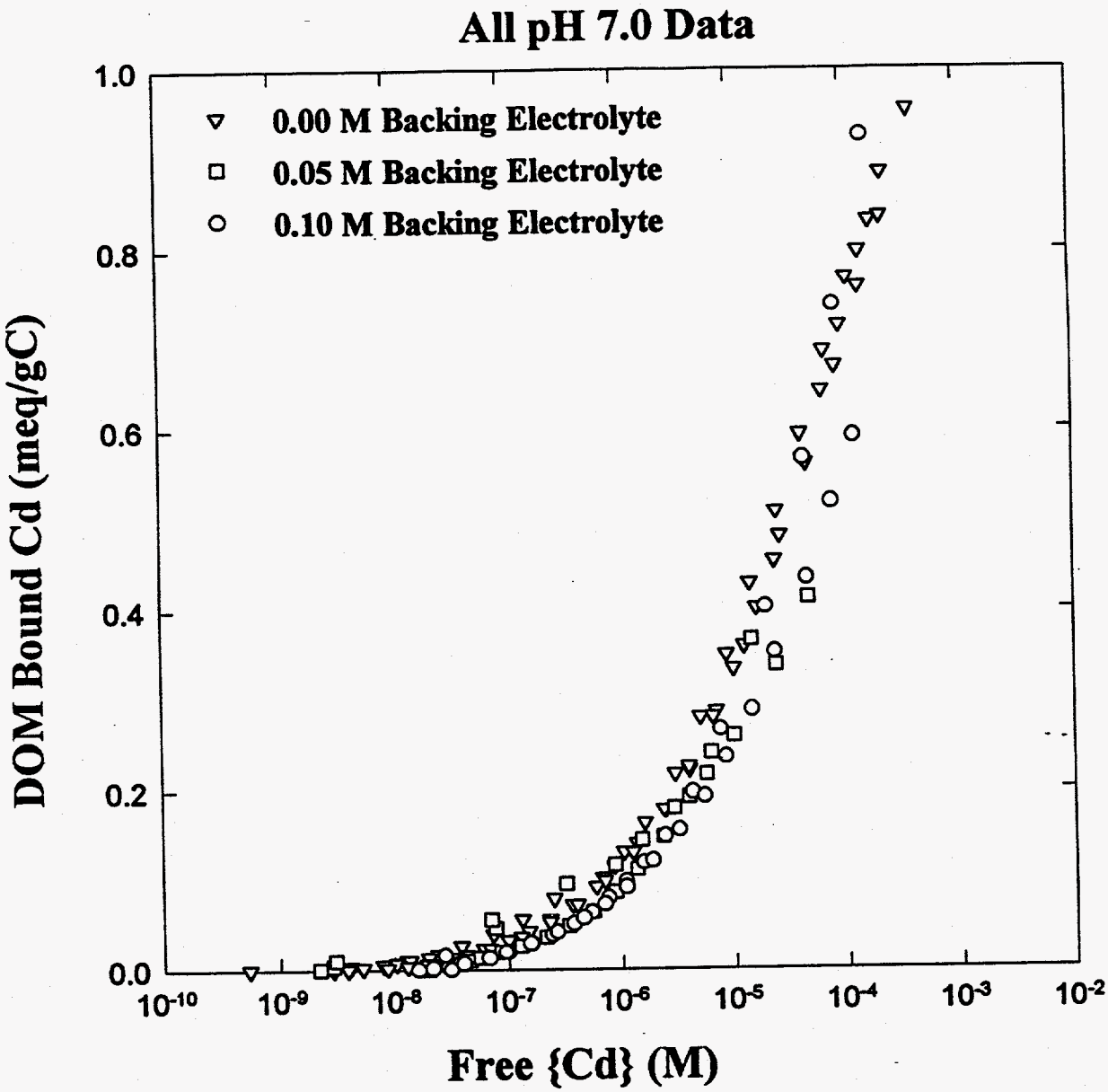


Figure 4-12. DOM bound cadmium as a function of free cadmium at 0 M backing electrolyte over all experimental pH values

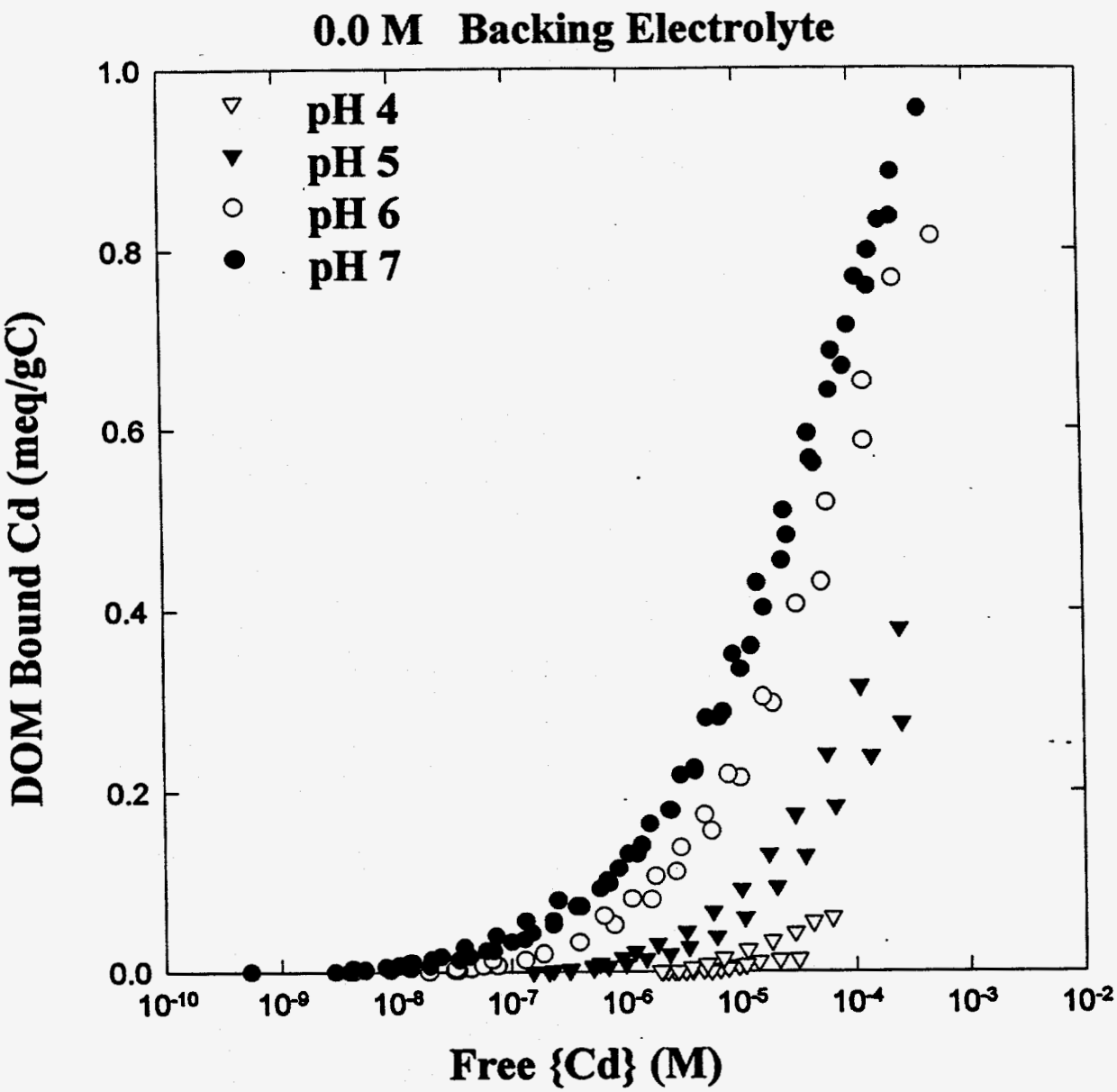


Figure 4-13. DOM bound cadmium as a function of free cadmium at with 0.05 M backing electrolyte over all experimental pH values.

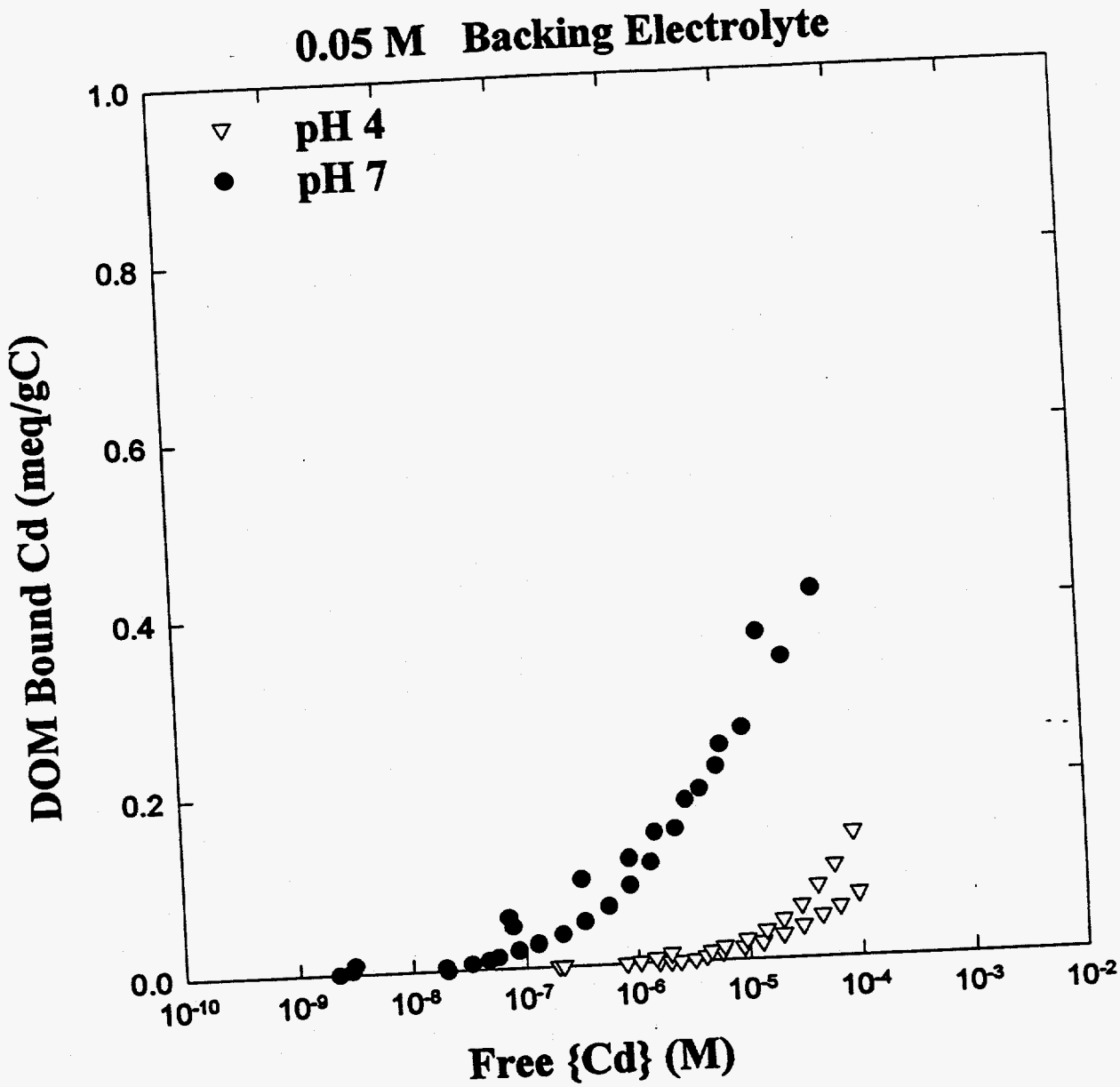


Figure 4-14. DOM bound cadmium as a function of free cadmium at with 0.1 M backing electrolyte over all experimental pH values

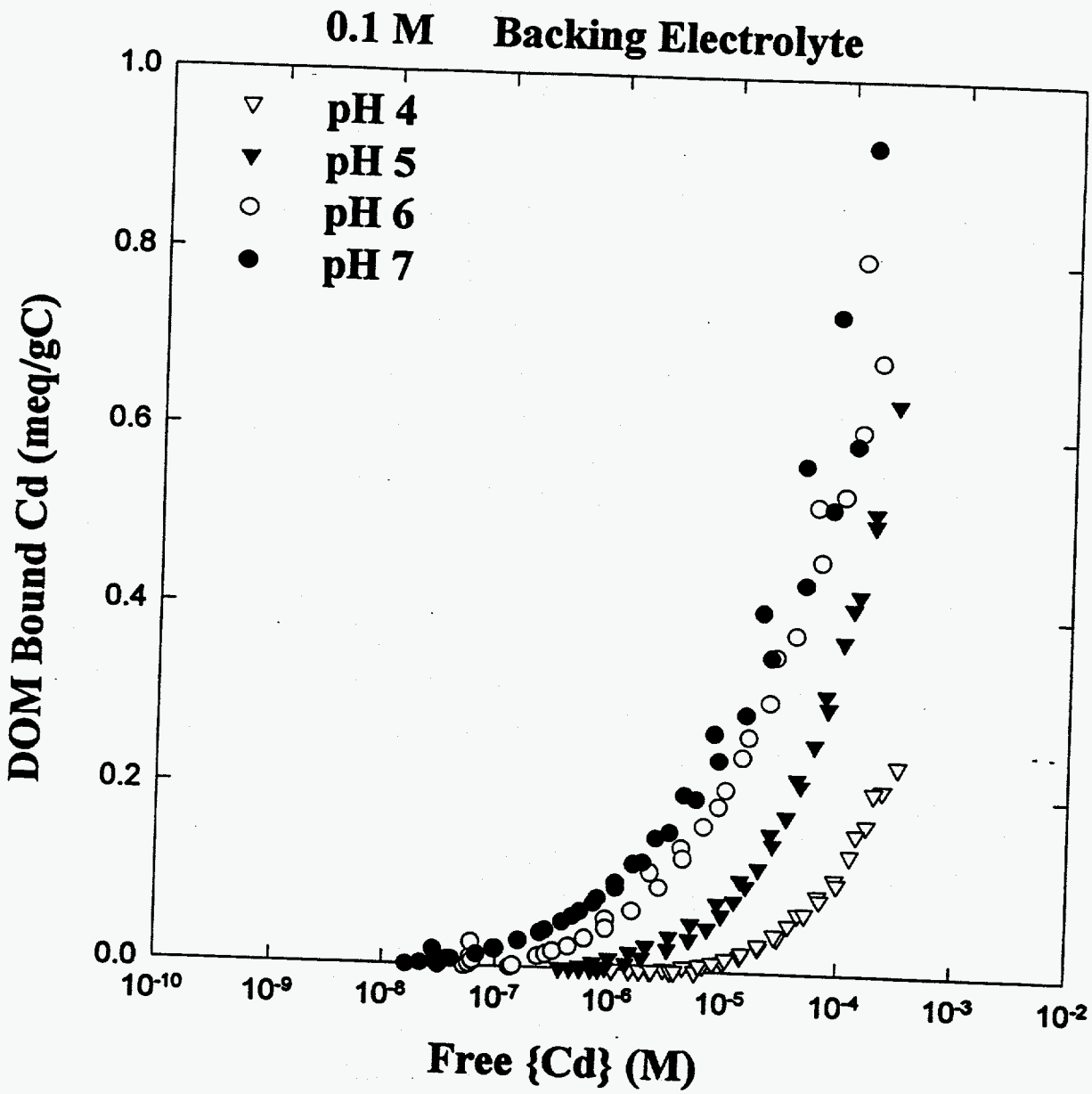


Figure 4-15. Comparison of model predicted and experimental data at pH 7 over all experimental ionic strengths

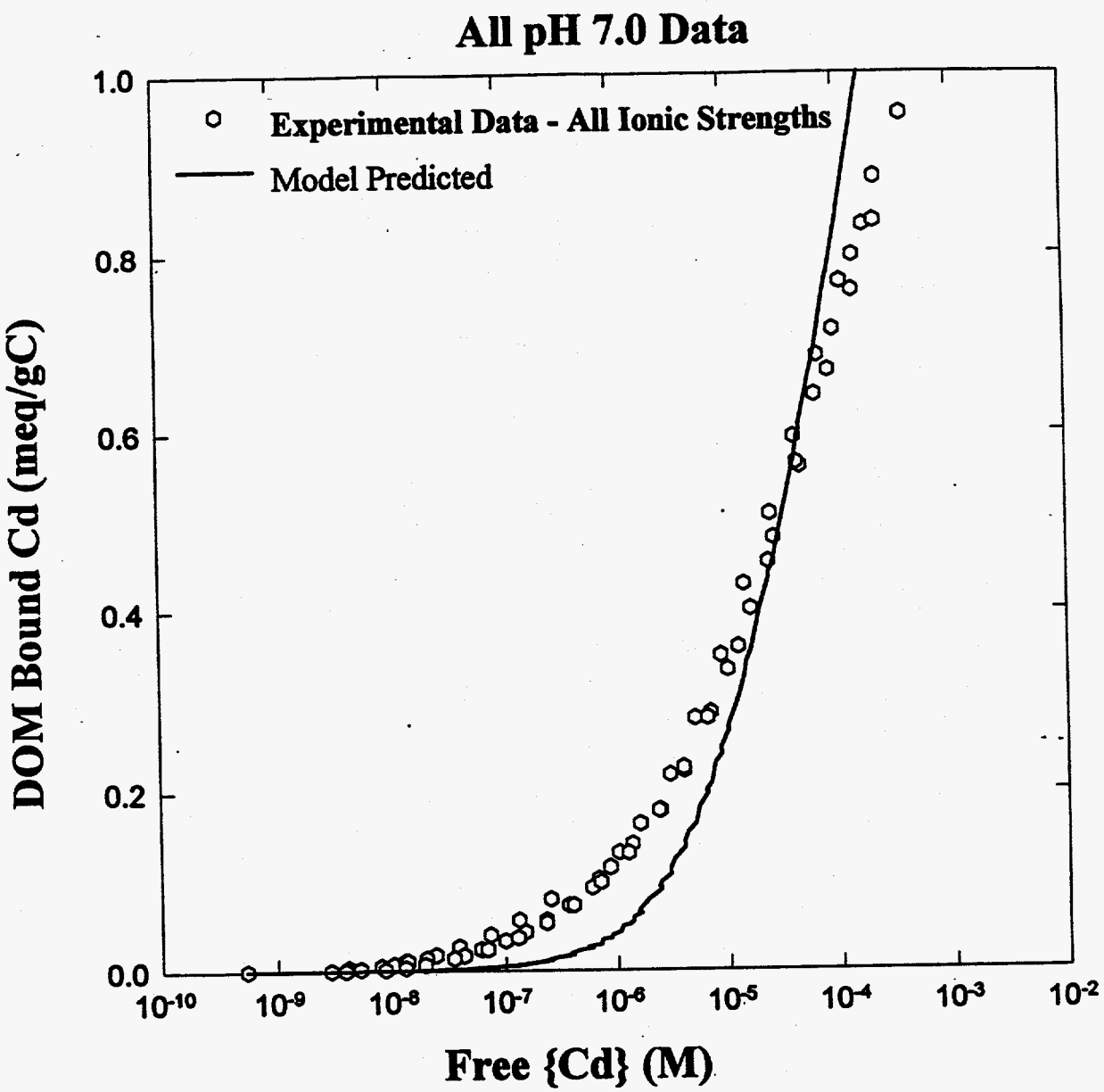
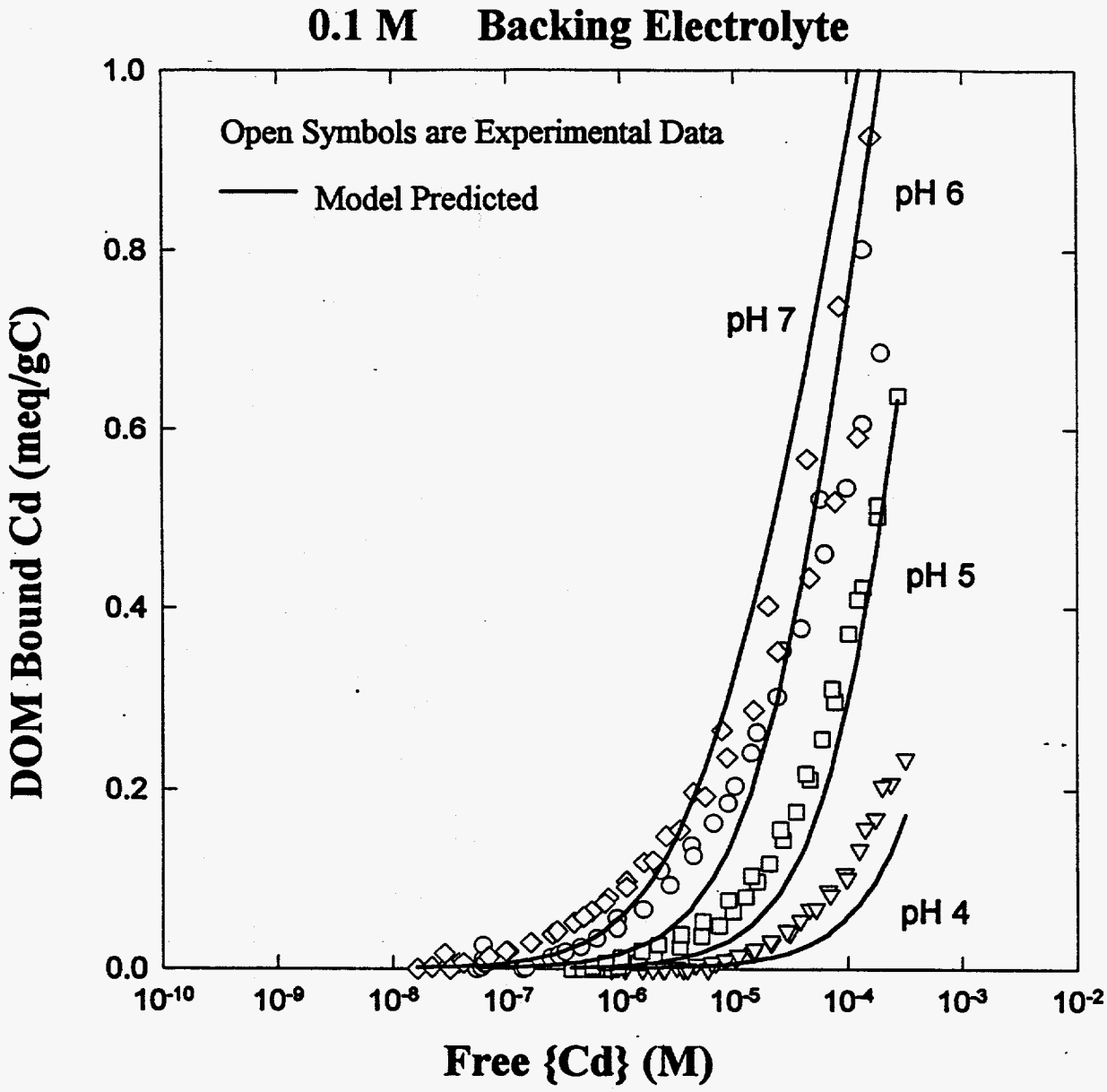


Figure 4-16. Comparison of model predicted and experimental data over all experimental pH values at 0.1 M backing electrolyte



5.0 CONCLUSIONS

The partitioning of a contaminant between the aqueous and solid phases in a natural system can not be accurately described by a single linear isotherm. A simple method of obtaining the actual distribution of contaminants in a polluted aquifer is to analyze sets of porewater and soil samples obtained at the same location in the aquifer, at the same time. The actual distribution coefficients of the FHSB system found using this method vary by two orders of magnitude.

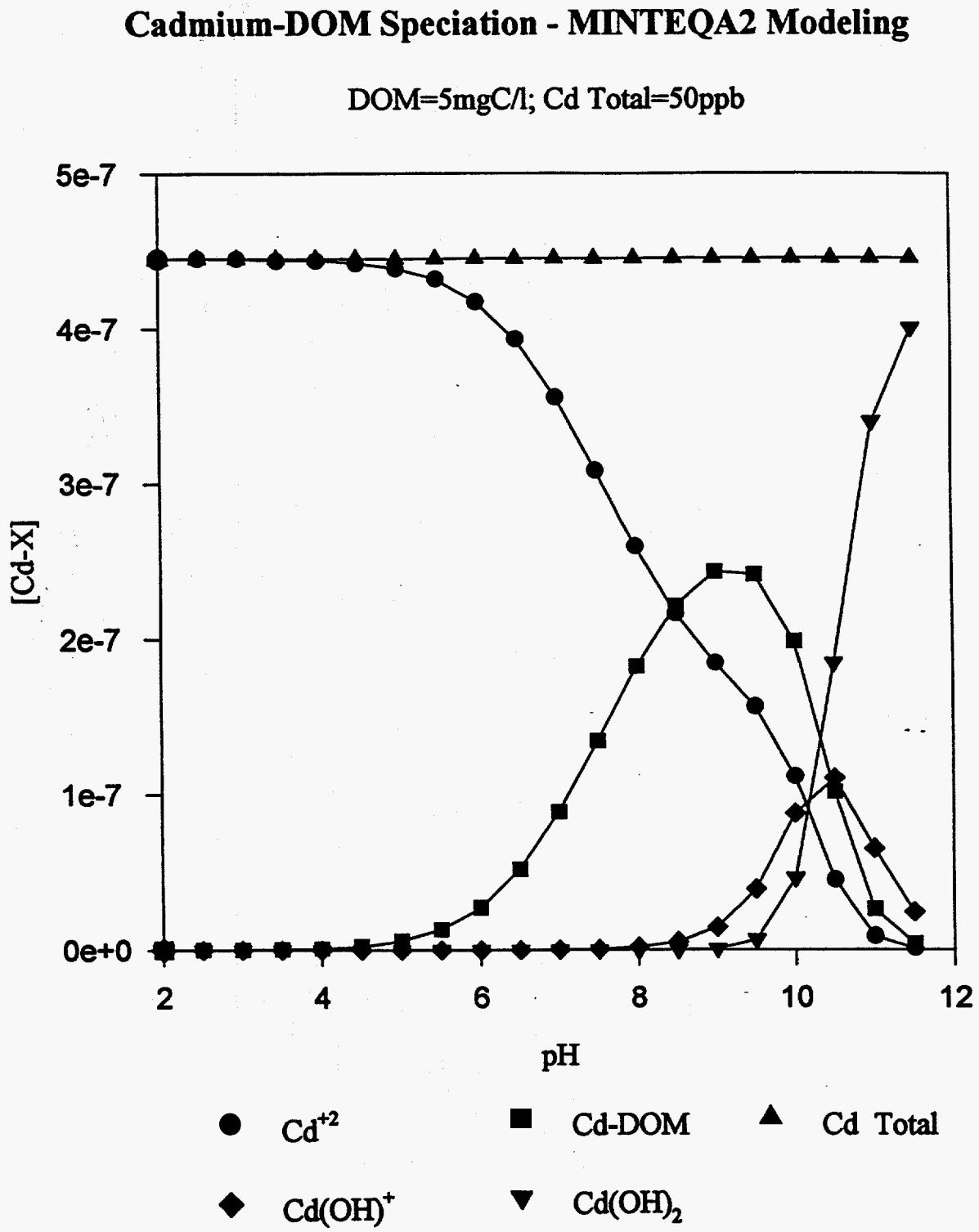
Aqueous phase speciation modeling predicts that cadmium should be present as the Cd^{2+} ion regardless of aqueous pH or redox potential. Because of the low aqueous concentration of cadmium and low aqueous pH values present at FHSB, precipitation of cadmium as cadmium compounds is not expected.

The partitioning behavior of cadmium to FHSB soils can not be explained in terms of the physical properties (i.e., particle size distribution, or cation exchange capacity). Laboratory studies show that cadmium is not sorbed when aqueous pH is less than 4.5. Above pH 4.5, there is a increase in cadmium sorption.

The competitive Gaussian distribution model was able to describe the binding of cadmium to naturally occurring DOM over an environmentally realistic range of ionic strengths (from about rain water to sea water) and pHs with a single stability constant. This means that this constant is <u>not</u> conditional on pH and ionic strengths and, therefore, should represent a significant improvement when modeling systems where the geochemistry is dynamic.

Because the competitive Gaussian distribution model has been implemented into MINTEQA2, the EPA's metal speciation model, as the means to model DOM metal interactions, this model has been updated to include the cadmium binding stability constants from this work to simulate real world geochemical systems containing cadmium and DOM. At the FHSB, currently, the DOM concentrations are about 2-5 mg l^{-1} and the maximum observed cadmium concentrations are about 50 ppb. A MINTEQA2 simulation was completed for conditions of 50 $\mu g\ l^{-1}$ cadmium and 5 mg l^{-1} DOM to illustrate the effect of DOM on cadmium speciation at the FHSB. The results are presented in Figure 5.1 and indicate that the cadmium-DOM complex is unimportant until pH values greater than 7. Therefore, cadmium-DOM interactions are probably currently unimportant at the FHSB.

Figure 5-1. Cadmium speciation versus pH for a system with 50 µg l^{-1} cadmium and 5 mg l^{-1} DOM



6.0 IMPLICATIONS FOR REMEDIATION AND RECOMMENDATIONS

6.1 Further Work

Knowledge of the types of soil binding sites to which cadmium sorbs can lead to a more accurate prediction of cadmium transport. In a future study, the sorption of cadmium onto 8 operationally defined "classes" of binding sites will be examined. In this study, a small portion of each soil sample will be sequentially leached using increasingy aggressive extractants. The contaminants removed with each extractant, will be classified as belonging to a given "class" of binding site. The 8 extractants and associated classes of sites are as follows:

1) Water soluble constituents which can be removed by shaking in deionized water for 16 hours;
2) Easily exchangeable constituents removed using 0.5 M $Ca(NO_3)_2$ solution (16 hours);
3) Specifically sorbed constituents which can be removed from the soil surfaces by a solution of 0.44 M CH_3COOH and 0.1 $Ca(NO_3)_2$ (8 hours);
4) Contaminants associated with easily reducible metals such as ferrous iron and manganese oxides removed with a solution of 0.01 M NH_2OH-HCl and 0.1 M HNO_3 (30 minutes);
5) Organically bound contaminants extracted with 0.1 M $Na_4P_2O_7$ (24 hours).
6) Contaminants sorbed on the poorly crystalline aluminosilicates and hydrous oxides extracted using a 0.175 M $(NH_4)_2C_2O_2$/0.1 M $C_2H_2O_4$ solution in the dark (4 hours).
7) Contaminants associated with crystalline iron oxides which can be removed by reducing Fe^{3+} to Fe^{2+} with 0.75 g $Na_2S_2O_4$ and while complexing the ferrous iron in a citrate solution made with 0.15 M $Na_3C_6H_5O_7$ and 0.05 M $HOC(CH_2CO_2H)_2CO_2H$ (30 minutes).
8) Residual constituents removed by a digestion in hot hydrofluoric acid and aqua regia. For this step, between 100 - 200 mg of oven-dried residue are placed in Teflon inserts with 1 ml of ultra-pure aqua regia and 10 ml of ultra-pure HF. The inserts are then placed in acid digestion bombs and heated at 105°C for 3 hours. The resulting extracts are filtered either through 0.45 µm Teflon syringe filters or Whatman 42 filter paper (2.5 µm), and diluted to 50 ml with deionized water.

The extractants from each step of the sequential extraction procedure will be analyzed using inductively coupled plasma-mass spectrometry (ICP-MS) to determine the concentrations of desired isotopes. A mass balance check of the sequential extraction procedure may performed by comparing the concentration determined by the total digestion to the sum of the concentrations extracted in all of the sequential extraction steps

Extension of these data to other waste sites through quantifying types of soil sorption sit should be attempted. Operationally defined classes of binding sites, like those being used in the above described sequential extraction experiments, should provide a method to accomplish this.

The distribution coefficients reported in this work tend to overestimate cadmium sorption because the cadmium concentrations reported in the soil included not only the cadmium sorbed on the soil surface, but also that associated with the soil matrix. The sequential extraction procedure described above allow better estimates of the true cadmium partitioning. By assuming that only that cadmium released with the final extraction is associated with the soil matrix, an more representative K_d value can be estimated.

6.2 Implications for Remediation

Based on the analysis of data from this study, cadmium in the water and soil at the FHSB does not require remediation. The few instances of elevated cadmium concentration observed are expected to be self correcting to background concentrations without any remedial assistance. The K_d value of six used in the previous groundwater modeling effort (GeoTrans 1991) is in fairly good agreement with the best fit K_d from the field-derived sorption data of 13.

Currently, only five of the 54 (9 percent) porewater samples collected in the Watertable Aquifer at the FHSB exhibited cadmium concentrations over the regulatory limit of 5 $\mu g\ l^{-1}$. The maximum concentration observed was 23.5 $\mu g\ l^{-1}$ and all samples with cadmium above the GWPS had pH values below 4. Soil concentrations of cadmium downgradient of the seepage basins are on average lower and not statistically different from those obtained for background samples collected in an unimpacted area upgradient of the basins. These soil concentrations are consistent with data reported by Looney et al. (1990) of a mean value less than 600 $\mu g\ l^{-1}$.

The slightly lower soil concentrations downgradient of the basins and the laboratory performed alteration study of the background soil with a simulated low-pH waste showing the release of cadmium from the soil matrix, suggest that the aqueous cadmium observed in the groundwater is largely due to the leaching of cadmium from the natural soil matrix. Because aqueous concentrations of cadmium are below or very near the GWPS of 5$\mu g\ l^{-1}$ and it is anticipated that the increased sorption and decreased leaching will occur as the pH of the system continues to increase, the groundwater system at FHSB is expected to naturally reduce cadmium concentrations to below the regulatory limit even in the absence of remediation.

DOM-cadmium interactions could increase the concentration of cadmium in the porewater. However, based on experimental and modeling results , the increase is not

expected to be significant. If, however, the pH of the system rises to above eight or DOM concentrations increase significantly, then DOM-cadmium interactions could become significant.

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