In-Situ Kd Values nad Geochemical Behavior for Inorganic and Organic Constituents of Concern at the TNX Outfall Delta

by

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TNX, metals, radionuclides,
sequential extractions, colloids

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**In-Situ K_d Values and Geochemical Behavior for Inorganic and Organic
Constituents of Concern at the TNX Outfall Delta (U)**

January 21, 2000

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Authorized Derivative Classifier

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Executive Summary

A series of tests were conducted to provide site-specific K_d values for constituents of concern (COCs) at the TNX Outfall Delta Operable Unit (TNXOD OU). These K_d values can be used to calculate contaminant migration within the operable unit and are, at this time considered to be the most defensible values. Additional sequential extraction tests were conducted to evaluate the "environmental availability" (i.e., the strength that the contaminants are associated with sediments) of COCs sorbed to the site's sediments. This concept was subsequently used to determine which sediment fractions were responsible for COC sorption. These latter tests provided important supporting data for technically defending the selected "Reasonably Conservative" K_d estimates.

K_d values were determined primarily by desorption measurements of contaminated sediments collected from the study site. For those COCs that were not present in the sediment samples, K_d values were determined either by sorption (which includes adsorption, absorption, and precipitation) tests or by using a common EPA-approved method based on literature-derived organic matter/water partition coefficients (K_{om}). Based on its intended use, the desorption K_d test provides the best measure of contaminant association with the site's sediment because the desorption process typically controls solute transport more than the sorption process. Additionally, unlike the sorption tests, desorption tests capture the contaminant "aging" process within the sediment. Some of the COCs had been in contact with the sediments used in this study for greater than 30 years. The desorption K_d values were based on extractable portions that were comprised of the "exchangeable," "organic-bound," the "amorphous Fe-oxide bound," and the "saturated-paste, water extractable" fractions. These sediment fractions are more likely to sorb or desorb contaminants than the fraction of the COC inside the mineral or crystalline Fe-oxide structure. By basing the K_d estimates on these extractable fractions, instead of the more easily determined total-concentrations in the sediment, more conservative and technically defensible K_d values were measured. "Reasonably Conservative" and "Upper Limit" K_d values were estimated based on sorption and desorption tests and were based on the lowest and highest measured values, respectively (see table below).

In general, most of the in-situ K_d values were appreciably larger than default conservative K_d values used in previous contaminant transport calculations. In the case of the desorption experiments, the cause for the large values can in part be attributed to the contaminants having several years to "age" with the sediments. During the aging process, the sorbed contaminants may be incorporated into the structure of the solid phase or be buried on the solid phase beneath recently formed precipitates, thereby limiting re-entry into the mobile aqueous phase. The organic-COC K_d values were generally quite low. This may be attributed to the implicit assumption associated with the calculation that sorption occurs only by partitioning to the organic matter and not to the mineral phase. This assumption is increasingly inaccurate as the hydrophobicity of organic solute and the mineral surface area increases.

The sequential extraction experiment revealed that Cu, Hg, and Pb were strongly bound onto the sediment, providing supporting evidence for selecting large K_d values for these COCs.

Conversely, Cd, Cr, Co, and Tl, tended to be associated with the "exchangeable" and "organically bound" fractions, suggesting that lower K_d values be selected for these COCs. COC concentrations were measured in the whole sediment, the <2- μ m fraction, and the <0.5- μ m fractions. The motivation behind this work was the hypothesis that some of the less soluble COCs, such as Th and Hg, may have been transported at the study site via association with mobile particles (including colloids). Among the most contaminated sediments, there was only sporadic evidence of contaminant-concentration enrichment in the smaller fractions. These data do not rule out the possibility that COCs may be moving via particulate transport, but do strongly suggest that particulates are not the only means for transporting the COCs.

The sequential extraction and the COC concentration versus size fraction data also have important implications for the selection of remediation strategies. Due to their greater environmental availability, Cd, Cr, Co, Tl, Th, and U are more likely to be remediated by phytoremediation or solvent extraction than Cu, Pb, and Hg. Conversely, Cu, Pb, and Hg would make better candidate contaminants for monitored natural attenuation than Cd, Cr, Co, Tl, Th, and U. The COC concentration versus size fraction data suggested that soil washing, which removes the smaller size fraction of contaminated sediments, would not be an effective strategy for remediating these sediments.

Reasonably-Conservative and Upper Limit K _d Estimates Based on in-situ, K _d Measurements Made From Contaminated TNX Outfall Delta Sediments.					
COC	K _d (mL/g)		COC	K _d (mL/g)	
	Reasonably Conservative	Upper-Limit		Reasonably Conservative	Upper-Limit
Ac	255	4074	Ni	257	404
Ag	>233	>1947	Pb	>11460	>38751
Al	228	1930	Pm	255	4074
As	55	592	Ra	336	392.7
Ba	320	374	Se	219	267
Be	45	181	Sr	1676	5518
Cd	39	39	Tc	0.5	12.5
Ce	255	4074	Tl	41	75
Cm	255	4074	Th	115	2255
Cr	58	2062	U	170	6493
Cu	67	290	cis-1,2-Dichloroethene	0	0.1
Fe	199	2589	Trichloroethene	0.1	0.2
Hg	4704	5725	Carbon Tetrachloride	0.2	0.2
K	1.2	3.2	Tetrachloroethene	0.6	0.9
Mn	268	3108	Vinyl Chloride	0	0.1

In summary, this study provided technically defensible evidence for selecting several K_d values, especially for the inorganic COCs, which are appreciably greater than present literature-derived values. These site-specific values will improve accuracy and remove some unnecessary

conservatism in future transport and risk calculations associated with the TNX Outfall Delta Operable Unit.

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1. Introduction

1.1. Sorption and Desorption Kd Values

The distribution coefficient, or Kd value, is one of the simplest constructs that describes contaminant sorption to sediments. It is the ratio of the contaminant concentration sorbed to the solid phase divided by the contaminant concentration in the liquid surrounding the solid phase (Equation 1):

$$Kd = \frac{C_{solid}}{C_{liquid}} \quad (1)$$

where C_{solid} ($M\ kg^{-1}$) and C_{liquid} ($M\ L^{-1}$) are the contaminant concentration in the solid and liquid phases, respectively. The Kd value is commonly used to define the retardation factor, which is the ratio of the average linear velocity of water ($m\ s^{-1}$) divided by the average linear velocity of the contaminant ($m\ s^{-1}$). The Kd value is related to the retardation factor (Rf , unitless) by the bulk density (ρ_b , $kg\ m^{-3}$) and the porosity (η , $m^3\ m^{-3}$), as shown in Equation 2 (Valocchi 1984, Bouwer 1991):

$$Rf = \left(1 + \frac{Kd\rho_b}{\eta} \right) \quad (2)$$

There are several implicit assumptions involved in using the Kd value in Equation 2 (reviewed by Bouwer 1991). Among these assumptions is that the rate of adsorption is equal to the rate of desorption. In natural sediments, this is rarely the case because desorption processes are almost always appreciably slower than the sorption process (Sposito 1994). Furthermore, the longer a contaminant is in contact with the sediment, the greater the sorption/desorption hysteresis. As the contaminant "ages" with the sediment, the contaminant becomes more refractory by 1) diffusing deeper into the structure of the solid phase, or 2) being buried under surface precipitated layers. This latter process is especially common in carbonate systems (Sposito 1994) and may also occur in Fe- and Al-oxide systems, the system at the SRS. Consequently, Kd values measured via sorption laboratory methods typically are appreciably less than Kd values measured via desorption methods. The former technique typically does not capture the "aging" phenomenon.

Kd values measured by sorption methods, henceforth referred to as sorption Kd values, are measured and used appreciably more often than desorption methods. There are several reasons for this. Geochemists are often interested only in the mechanisms and the conditions affecting contaminant sorption; the ultimate use of their data is not for contaminant transport calculations. Another reason for measuring sorption Kd values is that it is appreciably easier to do than desorption Kd values. For sorption Kd values, a known concentration of the contaminant is added to an uncontaminated solid phase. Assumptions about the speciation of the spiked contaminant must be made. The difference in the aqueous phase concentration before and after

equilibration with the solid phase is assumed to be the contaminant concentration sorbed to the solid phase, as illustrated in Equation 3.

$$Kd_{sorption} = \frac{(C_i - C_f) \times \left(\frac{V_{aq}}{M_{sed}} \right)}{C_f} \quad (3)$$

where i and C_f are the initial and final contaminant concentration in the aqueous phase, V_{aq} is the volume of the aqueous phase, and M_{sed} is the mass of the solid phase.

Desorption Kd values, as compared to sorption Kd values, capture many processes that are more important to contaminant transport. Most sorption processes occur in the time frame of seconds to weeks. Natural desorption processes occur in the time frame of years to hundreds of years, which is similar to the time frame of interest for most transport modeling efforts. Perhaps just as important, desorption, as compared to sorption, is often the rate limiting process governing geochemical behavior in sediments. This latter point is important because it implies that contaminant transport is more likely controlled by desorption than adsorption.

Unfortunately, desorption Kd values are appreciably more difficult to measure than sorption Kd values. The difficulty lies in defining the contaminant concentration associated with the solid phase, C_{solid} in Equation 1. As mentioned above, the Kd construct describes the linear and completely reversible sorption of a contaminant to a sediment. The term "linear" indicates that the aqueous contaminant concentration does not influence the degree of sorption. The term "reversible" indicates that the rate of sorption is equal to the rate of desorption. The value that is used in the numerator of a Kd , C_{solid} , must reflect not the total amount of contaminant in the sediment, but the reversibly sorbed contaminant concentration. Contaminants that have become part of a mineral structure or have coprecipitated from solution have little chance of re-entering the aqueous phase. These refractory contaminants should not be included in C_{solid} or an unrealistically high Kd will be measured. Unfortunately, the totally reversibly sorbed fraction is appreciably more poorly defined than the total contaminant concentration associated with the solid phase.

1.2. Selective Contaminants Desorption from Sediments

It is common for a contaminant to sorb by several processes at the same time when put in contact with a natural heterogeneous sediment. Furthermore, the rate that a contaminant sorbs and desorbs from an assembly of solid phases in a natural sediment varies. For example, cation exchange generally occurs appreciably faster than precipitation (Sposito 1994). Also, sorption and desorption rates of many cation exchange reactions are almost identical (Serne et al. 1996), whereas sorption and desorption rates of surface complexation reactions typically exhibit a large hysteresis (Sposito 1994).

Theoretically, when the K_d values is used to define the retardation factor (Equation 2), it almost exclusively describes contaminant sorption and desorption by cation exchange. However, sediment K_d values measured in the laboratory almost always include sorption by other processes. Thus, the operational definition of a K_d provided in Equation 3 is not theoretically correct because sorption processes, other than those that are reversible are measured by this technique.

Numerous studies have been conducted to identify extraction techniques that selectively desorb specifically defined sediment fractions (Tessier et al. 1979, Miller et al. 1986, Nirel and Morel 1990, Clark et al. 1996). Typically, contaminants are desorbed from sediments by a sequential series of progressively more-aggressive extractants. Each extractant targets either a particular sorption process, such as cation exchange, or a particular phase within the heterogeneous sediment sample, such as the organic or amorphous Fe oxide phase.

Among the more important sorptive phases in the sediments in the TNX Outfall Delta are amorphous and crystalline Fe/Al oxides, organic matter, and minerals (primarily quartz, kaolinite, hydroxy-interlayered vermiculite, and illites). Among the more important sorption mechanisms are:

- surface complexation onto pH-dependent charge sites on Fe and Al oxides, natural organic matter, and kaolinite,
- cation exchange onto permanent charge sites of minerals, and
- coprecipitation into Fe and Al oxides.

1.3. Objectives and Scope

The objectives of this study were to:

1. measure in-situ K_d values for several inorganic constituents of concern (COCs),
2. calculate K_d values for several organic COCs using measured organic matter concentration data and literature-derived organic matter/water partition coefficients, K_{om} .
3. conduct sequential extractions to evaluate the environmental availability of COCs and to evaluate which sediment phases are responsible for sorption, and
4. determine if the COC concentrations are enriched in the smaller particles, thereby making it possible for mobile particulates, including colloids, to enhance COC transport at the site.

The COCs at this waste unit were aluminum, arsenic, barium, beryllium, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, selenium, silver, thallium, actinium, cerium, curium, potassium, promethium, radium, strontium, technetium, thorium, uranium, cis-1,2-dichloroethene, trichloroethene, carbon tetrachloride, tetrachloroethene, and vinyl chloride. Samples from five contaminated and one uncontaminated sediment locations from the TNX Outfall Delta area were used in this studies.

2. Materials and Methods

2.1. Sediment Characterization

Five contaminated and one uncontaminated (background:101, BG5-0) sediment from the TNX OD were used in this study (Table 1). The sediments were collected by a private contractor using a hand auger and delivered to our laboratory through standard Chain of Custody protocol. The contaminated sediments were selected because it was anticipated that they would have high contaminant concentrations based on contamination maps previously reported. Sediment 101, BG5-0, was collected from an uncontaminated portion of the study area. The sediment from the 0 to 0.4-ft depth at this location consisted primarily of organic matter. This 0.4 to 1.4-ft depth sample was selected because its higher mineral content was more typical of the contaminated sediments (Sediments 102 – 106). The criteria used for selecting the location and sampling depths of the contaminated samples was to obtain sediments that were highly contaminated with a wide range of contaminants. The total COC sediment concentration data reported in WSRC-RP-98-4158, Rev. 0 ("RFI/RI with BRA for the TNX Outfall Delta, Lower Discharge Gully and Swamp Operable Unit," July 1999) was used as the basis for identifying the location and sampling depths. Finally, the reason for selecting sediment 105 was slightly different from the other contaminated samples. This location, D28, was selected because it was far from the point source and it had high contaminant concentrations, i.e., it was a "hot spot" far from the point source. This sample was used, along with the others, to evaluate whether particulate/colloid transport occurred at the site.

Table 1. Sediment identification and description.

Chain of Custody ID#	Chain of Custody Description	Sample Depth (ft)	Expt. ID#, Description
119329	TNXOD-BG5K	0.4 to 1.4	101, BG5-0
119312	TNXOD-A5K	0 to 1	102, A5-0
119316	TNXOD-B5K	0.5 to 1	103, B5-0.5
119321	TNXOD-C5K	1 to 2	104, C5-1
119322	TNXOD-D28K	0 to 1	105, D28-0
119325	TNXOD-B3K	0.2 to 0.5	106, B3-0

Soil pH was determined on 1:1 soil/water equilibrations (Thomas 1996). Soil organic C was determined by a modification of the unheated potassium dichromate method (Nelson and Sommers 1982). Cation and anion exchange capacities were determined by exchange with potassium and nitrate ions on sediments that were not pH adjusted, following the method of Sumner and Miller (1996). Iron oxide concentrations were determined by the dithionite reduction procedure (Loeppert and Inskeep 1996). Particle size distribution (sand, silt, and clay concentrations) was determined by the micropipette method (Miller and Miller 1987). Mineralogical semi-quantitative information was collected from X-ray diffraction analyses of the <2- μ m clay fraction that had been H₂O₂-treated for organic matter removal. X-ray diffraction

was conducted on Mg-saturated samples that had been sequentially analyzed at 25° C, then again after the clay mount had been treated for 16 hr at 65° C, and then treatment for 16 hr at 300° C.

Analytical precision was $\leq 3\%$ for the inductively coupled plasma-atomic emission spectroscopy, and $\leq 3\%$ for pH, specific conductivity, and organic C.

2.2. Overview of the Sequential Extraction Measurements

An overview of the sequential extraction procedure used in this study is presented below. Details of the procedure are presented in Appendix A.

The sequential extraction method used in this study was taken from Miller et al. (1986) and is a modification of ASTM method D 5074-90 (ASTM 1990a) and ASTM D-3974-81 (ASTM 1990b). Six extractions (Table 2) were made from each of the 6 sediments. The mass extracted in the first four extraction steps were used to calculate the desorption K_d values (described below).

In an attempt to quantify the fraction of contaminant associated with the mineral matrix, some researchers have turned to selective extraction techniques (Amonette 1994, Tessier et al. 1979). Importantly, these selective or sequential extraction techniques have experimental limitations (Tessier et al. 1979, Nirel and Morel 1990). Problems with sequential extractions include incomplete extraction of trace elements or mineral surfaces, non-selectivity of extraction reagents for given soil phases, or readsorption of extracted contaminants onto other surfaces. Thus, individual sequential extraction phases may not adequately represent the discrete soil phase to which the contaminant is bound. The actual concentration extracted may only be assumed associated with a given operationally defined phase.

Table 2. Sequential Extractants

Se- quence	Extractant: Chemical Composition	Targeted Contaminant Fraction	Ref. ^a
1	Saturated Paste Extract: uncontaminated TNX surface water	Aqueous	1
2	Dilute-acid Extract: dilute acetic acid [0.44 M CH_3COOH + 0.1 M $\text{Ca}(\text{NO}_3)_2$]	Exchangeable	2
3	Organically Bound Extract: sodium pyrophosphate [0.1 M ($\text{Na}_4\text{P}_2\text{O}_7$)]	Bound to Organic Fraction	2
4	Amorphous Fe-oxide Extract: acidified ammonium oxalate: pH 3 (0.175 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ + 0.1 M oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$))	Associated with amorphous Al- and Fe-oxide	2
5	Crystalline Fe-oxide: 3.33% Sodium dithionite in 0.15 M sodium citrate + 0.05 citric acid buffer	Associated with crystalline Al- and Fe-oxide	2
6	Aqua Regia: 1 part HNO_3 :3 parts HCl :1 part H_2O	Structural	2

^a References: 1 = Miller et al. 1986, 2 = Rhoades 1996.

The first extractant was the saturated paste. It was created by saturating a sediment with uncontaminated TNX surface water (collected about 1000-m north of the northern boundary of the TNXOD OU). The chemical composition of the uncontaminated surface water used in this study is presented in Table 3. The water was left in contact with the sediment for one week and the water was recovered and analyzed for the COC. The second extractant, a dilute acidic acid solution, targeted the exchangeable fraction (Table 2). The COCs associated with the sediment organic matter were recovered by dissolving (oxidizing) the organic matter with 0.1-M sodium pyrophosphate ($\text{Na}_4\text{O}_2\text{O}_7$). Sodium pyrophosphate is believed to oxidize the more readily oxidizable organic matter fraction, leaving organic matter that is harder to oxidize (i.e., organic matter high in lignin concentration). The COCs associated with the amorphous Fe-oxides were recovered by dissolving (reducing) this fraction with acidified ammonium oxalate. Ammonium oxalate will dissolve primarily the amorphous fraction, leaving behind the more crystalline fraction that requires a stronger reducing agent for it to dissolve. The COCs associated with the crystalline Fe-oxide fraction were recovered by dissolving the remaining solids with a stronger reducing agent than the ammonium oxalate, sodium dithionite. Finally, after the sediment had been treated with the five extracting solutions, it was totally digested. The COCs in the Aqua Regia digest were operationally assigned to be part of the mineral structure. This fraction is the least likely to contribute to the sorption/desorption process and contribute to COCs entering the mobile aqueous phase.

Table 3. Chemical Composition of Uncontaminated Surface Water Collected from near the TNXOD OU.^a

Constituent	Concentration (µg/L)	Concentration (mM)	Constituent	Concentration (µg/L)	Concentration (mM)
pH	5.1 (unitless)		Na	357.28	0.016
Al	9.12	0.00034	Ni	1.29	2.2E-05
As	<0.18		Se	<0.61	
Ba	64.87	0.0005	Si	4395	0.1565
Ca	3850	0.0962	Sr	33.98	0.00039
Ce	0.087	6.2E-07	Th	0.013	5.69E-08
Co	0.065	1.1E-06	Tl	0.055	2.69E-07
Cr	<0.92		U	<0.01	
Cs	0.052	3.9E-07	Chloride	2061	0.0598
Cu	<0.13		Nitrate	186	0.003
Eu	0.016	1E-07	Phosphate	<100	
Fe	99.3662	0.00178	Nitrite	<100	
Hg	0.076	3.8E-07	Sulfate	13690	0.214
K	229.15	0.0058	Inorganic C	<100	
Mg	1117.89	0.046	Organic C	6051	0.504
Mn	57.9	0.001	Summation of Cations		0.325
			Summation of Anions		0.277

^a Surface water sample collected about 1000-m north of the northern boundary of the operable unit.

2.3. Desorption Kd Values

Desorption Kd values (Kd_{desorb}) were measured from the six sediments used in the sequential extraction experiment (Table 1). The Kd values were calculated from the results of the first four extracts (Table 2) and were calculated using Equation 4:

$$Kd_{desorb} = \frac{C_{Acid} + C_{Org} + C_{AmFeOx}}{C_{Sat.Paste}} \quad (4)$$

where C_{Acid} , C_{Org} , and C_{AmFeOx} are the contaminant concentrations in the solid phase extracted by the dilute-acid extract, organically bound extract, and the amorphous Fe-oxide extract (µg/g), respectively, and $C_{Sat.Paste}$ is the contaminant concentration in the aqueous phase extracted from the saturated paste extract (µg/mL). The contaminant concentration in the aqueous phase, C_{liquid} , the denominator of the Kd term (Equations 1 and 4), was assumed to be equal to the amount of contaminant extracted by the saturated paste extract, i.e., TNX surface water left in contact with a field moist sample for 7 days. For additional details on how the saturated paste extract was prepared, see Appendix A. The C_{solid} of the Kd term (Equations 1 and 4) was assumed to be

equal to the exchangeable fraction plus the organic-bound fraction plus the amorphous Fe-oxide fraction as defined by the extracts presented in Table 2. The organic-bound extract, as the name implies, provides a measure of the amount of contaminant associated with the naturally occurring organic matter in the sediment by oxidizing the organic matter, thereby releasing the contaminant. The amorphous Fe-oxide extract provides a measure of the amount of contaminant associated with the non-crystalline, amorphous sesquioxides in sediments by partially reducing and solubilizing Fe(III)-oxides in the sediment to aqueous Fe(II). This extract is not strong enough to dissolve crystalline Fe-oxides. Aluminum oxides associated with the crystalline and amorphous Fe-oxide phases would also be extracted by these two treatments. The three extracts used to define C_{solid} for the maximum K_d term are expected not to recover contaminants that are occluded in silicates, aluminosilicates, crystalline Fe-oxides, or Mn-oxides. It was felt that only the exchangeable, organically bound, and amorphous Fe-oxide fractions would contribute to future contaminant plumes in this area. It is important to note, that the less contaminant assumed to be associated with C_{solid} , the more conservative (lower) the K_d estimate (Equation 1) will be.

2.4. Sorption K_d Values

Sorption K_d values were obtained for COCs for which desorption K_d values could not be measured. Desorption K_d values could not be calculated for some COCs because they had below detection-limit concentrations in the various desorption extractant solutions. These COCs were technetium, mercury, thallium, potassium, and barium (as a non-radioactive analog for radium). The batch sorption method used in these studies was based on ASTM method D 4319 (ASTM 1984). A detailed description of the method and the solutions made for these tests are presented in Appendix B. A brief description of the procedure follows.

The sediment used in this study was collected several hundred meters from the northern border of the TNXOD OU (Chain of Custody # TNXOD-BG5K or SRTC Sediment #101). Characterization of this sediment is presented in the Results and Discussion Section. For each element, approximately 0.35-g of sediment were placed in 40-mL centrifuge tubes. The sediments were then preequilibrated with 3 2-hr washes of uncontaminated TNX surface water (Table 2). For K, which already exists in the uncontaminated TNX surface water, the sediments used in the K sorption test was preequilibrated with 0.02 M NaNO_3 . Preequilibration of the sediments prior to conducting sorption tests has been shown to be essential (Kaplan and Serne 1999). Reactions, not of interest to the K_d measurement, such as precipitation, may occur as a result of the solution and sediment not being in equilibrium. The only solute that should be out of equilibrium during a sorption experiment is the solute of interest, in this case, the Hg, Ba, Tl, Tc, or K.

After preequilibration, 35-mL of uncontaminated TNX surface water was spiked with Ba, Hg, Tc (as $^{99}\text{TcO}_4^-$), or Tl and 0.02 M NaNO_3 was spiked with K. These spiked solutions were added to the preequilibrated sediments. Two concentrations of the spiked solutions were made for each solute: 643 and 7637 $\mu\text{g/L}$ Ba (from BaCl_2), 892 and 12,400 $\mu\text{g/L}$ Hg (from $\text{Hg}(\text{NO}_3)_2$), 1613 and 14900 $\mu\text{g/L}$ K (from KNO_3), 1.5 and 15 $\mu\text{Ci/L}$ Tc (from $^{99}\text{TcO}_4^-$ in carrier free stock), and 92 and 9800 $\mu\text{g/L}$ Tl (from TlNO_3). The spiked solutions were permitted to

equilibrate for three days prior to putting them in contact with the sediment. The soil-water suspensions were placed on a platform shaker for a week. After equilibration, the samples were centrifuged and then passed through a 0.45- μm filter. The filtrates were then analyzed by General Engineering Laboratories (Charleston, SC) for the solute of interest: Hg by cold vapor atomic absorption, K by atomic absorption, Tc by liquid scintillation counting, and Ba and Tl by ICP-ES. The concentration data were then used in Equation 5 to calculate $K_{d\text{sorb}}$ values. Equation 5 accounts for the dilution of the initial spike solution by the interstitial water remaining in the sediment after the final preequilibrating wash (i.e., the unspiked water left in the tube after washing):

$$K_{d\text{sorb}} = \frac{\left(\frac{(C_{\text{initial}} \times V_{\text{initial}}) - C_{\text{final}}(V_{\text{initial}} + V_{\text{interstitial}})}{M_{\text{sed}}} \right)}{C_{\text{final}}} \quad (5)$$

where $V_{\text{interstitial}}$ is the volume of the interstitial solution left after the third pre-equilibration wash (L), M_{sed} is the sediment mass (g), V_{initial} is the volume of the contaminant-amended solution added to the sediment (L), C_{final} is the contaminant concentration in the solution after contact with the sediment ($\mu\text{g/L}$), and C_{initial} is the contaminant concentration of the contaminant-amended solution ($\mu\text{g/L}$) added to the solids.

2.5. Organic Contaminant Kd Values Calculated from Water Partition Coefficients

Kd values for the organic constituents of concern were calculated, as opposed to measured directly, from organic matter/water partition coefficients, K_{om} values ([mg contaminant/g OM]/mg contaminant/mL water). The relationship between Kd and K_{om} is presented in Equation 6,

$$K_d = f_{\text{om}} K_{\text{om}} \quad (6)$$

where f_{om} is the weight fraction of natural organic mater (kg om/kg solid). There have been several theoretical and empirical relationships established between K_{om} and solubility and K_{om} and the octanol/water partition coefficient, K_{oc} (Schwarzenbach et al. 1993). Two such Linear Free Energy Relationships (LLER's) to K_{om} 's were used in this study. For the chlorinated hydrocarbon contaminants, cis-1,2-dichloroethene, trichloroethene, carbon tetrachloride, and vinyl chloride, Equation 7 was used:

$$\log(K_{\text{om}}) = -0.7\log(C^{\text{sat}}) + 0.35, \quad r^2 = 0.99 \quad (7)$$

where C^{sat} is the aqueous solubility of the neutral organic compound (Schwarzenbach et al. 1993). Equation 7 was established by using dozens of chlorinated hydrocarbon compounds. Thus, to calculate Kd values using Equations 7, one must measure the total organic carbon (natural organic matter consists of approximately 50% carbon) and literature values for C^{sat} . The

total organic matter concentrations and the literature input values for each compound are presented in Section 3.0, Results and Discussion.

2.6. Sample Analysis and Quality Assurance

The standard QA practices described in the WSRC QA Manual 1Q were followed throughout this study. Commercial computer software packages (e.g. Microsoft Excel) were used for calculations. The software calculations were validated and verified by hand calculations. All calculations are considered (General Service) GS calculations. All M&TE used in these experiments were calibrated by the Standards Laboratory. Calibration checks were performed by the section performing the work. Control of waste products from these activities were controlled by L1 Manual procedure 6.01.

3. Results and Discussion

3.1. Sediment Characterization

Properties of the sediments used in this study are presented in Table 4. The textures of the sediments varied substantially. The clay content varied from 6.3% for Sediment 101 to 19.4% for Sediment 103. The gravel fraction, >2-mm, was very small for all sediments except, Sediment 102, which contained 21.2% gravel.

The sediment pH of the 6 sediments varied by just short of 2 pH units, ranging from 4.00 to 5.78. The organic C concentrations were high, consistent with the fact that the sediments were collected from a forested wetland. The cation exchange capacity (CEC), a measure of the total number of cation exchange sites, was surprisingly low, considering that these sediments are high in organic C. Upland sediments on the SRS generally have CEC levels that are only fractionally lower than these values. The anion-exchange capacity (AEC) is a measure of the total number of anion exchange sites. These anion-exchange sites exist primarily on the organic matter and the Fe-oxides, but also exist to a smaller extent on the kaolinite particles. AEC ranged from $0.00 \pm 0.09 \text{ cmol}_{(-)} \text{ kg}^{-1}$ to $2.67 \pm 0.10 \text{ cmol}_{(-)} \text{ kg}^{-1}$.

Mineralogy of two fractions, <2- μm and <0.5- μm , of Sediments 105 and 106 is presented in Table 5. The dominant minerals were kaolinite and hydroxy-interlayered vermiculite, comprising >90% of the total mineral phase. Trace amounts of quartz, gibbsite, and illite made up the remainder of the mineral phase. This mineral composition is consistent with those previously reported (Ruhe and Matney 1990). The mineral composition of the <0.5- μm and the <2- μm fractions were remarkably similar (Figures 1 and 2). This finding is important in that it suggests that differences in contaminant association of these two size fractions would not be expected based on differences in mineralogy. For example, had the smaller fraction been dominated by illites or hydroxy-interlayered vermiculite, then greater contaminant association with the smaller fraction would be expected based on the greater sorption capacity of these minerals.

Table 4. Sediment Characterization^(a)

Sediment	<2-mm (%,wt)	Sand (%,wt)	Silt (%,wt)	Clay (%,wt)	pH	Org. C (mg/kg)	CEC (cmol ₍₊₎ /kg)	AEC (cmol ₍₋₎ /kg)	Fe-oxides ^(b) (%,wt)
101	0.8 ± 1.0	79.4 ± 2.1	13.6 ± 0.3	6.3 ± 0.8	4.16 ± 0.01	1395	4.75 ± 0.08	1.56 ± 0.17	0.01
102	21.2 ± 6.3	48.8 ± 6.8	23.6 ± 1.6	6.4 ± 1.1	4.00 ± 0.08	1493	8.96 ± 0.09	2.43 ± 0.05	0.08
103	5.9 ± 7.2	52.9 ± 8.2	21.8 ± 1.5	19.4 ± 0.6	4.53 ± 0.04	1427	7.33 ± 0.14	0.00 ± 0.06	0.09
104	1.5 ± 1.1	56.9 ± 0.4	31.4 ± 0.0	10.2 ± 0.7	5.26 ± 0.01	1167	9.31 ± 0.37	2.67 ± 0.10	0.10
105	2.6 ± 1.0	59.4 ± 4.4	257 ± 5.6	12.3 ± 0.2	4.29 ± 0.02	1435	7.83 ± 0.07	1.90 ± 0.04	0.07
106	0.5 ± 0.1	69.4 ± 0.3	19.9 ± 0.4	10.2 ± 0.2	5.78 ± 0.06	973	6.99 ± 0.06	1.50 ± 0.00	0.03

^(a) Analyses were conducted as duplicates or without duplication (where no standard deviation is presented).

^(b) Fe-oxides: extracted by Na-dithionite from total sediment (an estimate of concentration of Fe-oxide coatings); reported as % Fe₂O₃.

Table 5. Mineralogy of <2-um and <0.5-um Fractions^(a)

Sediment	Mineral	<2-um (%, wt)	<0.5-um (%, wt)
105	Kaolinite	68	75
	Quartz	0.8	0.2
	HIV ^(b)	24	21
	Illite	4.7	1.6
	Gibbsite	2.2	2.2
	Fe-oxides (as Fe ₂ O ₃)	0.1	Not Measured
106	Kaolinite	78	79
	Quartz	0.4	0.2
	HIV ^(b)	17	17
	Illite	1.9	2.6
	Gibbsite	2.3	1.9
	Fe-oxides (as Fe ₂ O ₃)	0.03	Not Measured

^(a) Semi-quantitative estimates based on x-ray diffraction analyses.

^(b) HIV = hydroxy-interlayered vermiculite.

Figure 1. X-ray diffractograms of the <2- μ m (top) and <0.5- μ m (bottom) fraction of Sediment 105. For each plot, the bottom, middle, and top diffractograms are for a 25°, 60°, and 300° C heat treatments, respectively. The peaks near 7°, 9°, 12°, 18°, and 27° 2-theta are for hydroxy-interlayered vermiculite, illite, kaolinite, gibbsite, and quartz, respectively.

Figure 2. X-ray diffractograms of the <2- μ m (top) and <0.5- μ m (bottom) fraction of Sediment 106. For each plot, the bottom, middle, and top diffractograms are for a 25°, 60°, and 300° C heat treatments, respectively. The peaks near 7°, 9°, 12°, 18°, and 27° 2-theta are for hydroxy-interlayered vermiculite, illite, kaolinite, gibbsite, and quartz, respectively.

3.2. Desorption Kd Values for Inorganic Contaminants

Desorption Kd values are presented in Table 7. The Conservative and Upper-limit Kd estimates presented in Table 7 are the lowest and the highest measured values. Kd values for Sediment 101, the uncontaminated sediment, are also included in this table, when their concentrations could be detected. The source of the contaminant is important because contaminants from natural sources may behave differently than those from anthropogenic sources, due to differences in concentration and speciation. Thus, in coming up with Reasonably Conservative and Upper Limit Kd values, the Kd values of Sediment 101, the background sediment, were not considered. No Kd values were calculated if C_{solid} and C_{liquid} had below detection values. Greater than Kd values were calculated if C_{solid} was measurable and C_{liquid} had a below detection value and a value of the detection limit was assumed for the C_{liquid} . Concentration data are presented in Appendix C.

Among the inorganic COCs, desorption Kd values were determined for Ag, Al, As, Ba, Be, Cd, Ce, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sr, Th, and U. COCs for which it was not possible to calculate Kd values due to below-detection-limit concentrations were Ac, Cm, Hg, Ra, Tl, and Pm. Below-detection-limit concentrations of Hg (0.010 mg/L) were surprising in light of the fact that Hg concentration maps of the area indicate as much as 15 mg/kg Hg existed in the areas where these sediment samples were collected. These latter COCs were not measured in an effort to meet schedule needs.

In general the Kd values are appreciably higher than the default literature Kd values used in contaminant transport calculations at the SRS. This can be attributed to: 1) desorption, rather than sorption being used to calculate the Kd values, 2) the high organic carbon concentrations of these sediments, and 3) the Kd values in these tables representing measured, site-specific values, instead of literature-derived conservative estimates, which are generally lower than measured values.

For several of the COCs, the variability was extremely high. This variability is likely real and not the result of experimental error. Among the more plausible causes for this variability is that the sediments appeared to differ greatly in texture, color, and organic matter content, hence they had different sorption properties (Table 4). Another probable cause for the variability is that the sources of the COCs may have been different, i.e., some COCs have natural and anthropogenic sources. Different sources may have different sorption processes. For instance, the concentrations of COCs from natural sources, such as U or Ce, may be limited by solubility constraints, whereas the concentration of the same COCs from anthropogenic sources, may be limited by (ad)sorption constraints.

An important caveat to this desorption data is that it is site-specific and that extrapolation to other sites is limited. Similar to traditional sorption Kd values, desorption Kd values are limited to systems with identical aqueous and solid phases. Thus, if conditions change at the field site, such as if the redox conditions change, it is expected that the Kd values for some of the

COCs may change. Also, desorption K_d 's are expected to change with time. So if a desorption K_d is measured shortly after a contaminant comes in contact with a sediment, the K_d value would be expected to be smaller than if it had been measured in a contaminated "aged" system. Consequently, the desorption K_d values reported in this report are likely greater than the K_d values that existed 30 years ago, when the contaminants first came into contact with the sediments. Finally, one important advantage of desorption K_d values that can not be over emphasized is that they do not require the experimenter make an assumption about the species existing in the system. In the case of sorption experiments, the experimenter must select a specie(s) to spike into the solid/liquid system.

Table 7. Desorption Kd Values (mL/g; Equation 4)

	Sediment						Reasonably Conservative ^(a)	Upper Limit ^(b)
	101	102	103	104	105	106		
Ag	>57	>346	>688	>234	>338	>1947	>233	>1947
As	(c)		592	55			55	592
Al	3369	1930	847	270	756	228	228	1930
Ba	98	6045	1231	326	1055	517	326	6045
Be ^(d)	45		181		159		45	181
Cd		39					39	39
Ce		2189	1523	255	4074	1361	255	4074
Cr	2411	1475	643	58	2062	1126	58	2062
Cu		290	169	67	313	86	67	290
Fe	4663	2589	1449	199	869	483	199	2589
Mn	24	3108	1889	328	268	319	268	3108
Ni		257	404	>59			257	404
Pb		>38751	>21068	>34511	>37610	>11460	>11460	>38751
Se	148	219	267	254	219	248	219	267
Sr	1048	5518	3515	1676	2190	1886	1676	5518
Th			1803	115	2255		115	2255
U-238		1237	1297	170	6493	2110	170	6493

^(a) Reasonably Conservative value is the lowest measured value among the contaminated sediments (Sediments 102 – 106).

^(b) Upper Limit Kd value is the largest measured value among the contaminated sediments (Sediments 102 – 106).

^(c) Empty cells in table indicate that no desorption value could be measured due to below detection limit concentration in the sample.

^(d) Be Kd values are estimated based on Ca desorption data. The Be Kd values reported in this table are half the measured Ca-Kd values. Based on periodicity consideration, it is anticipated that these divalent IIA-group elements will behave very similarly; Ca will sorb slightly more strongly than Be.

Simple Pearson Correlation Coefficients (Table 8) were calculated using the desorption Kd values in Table 7 and the soil characterization data presented in Table 4. Additional correlation coefficients between the various soil properties are presented in Appendix Table C5. Before describing the results of these calculations, it is important to remember that significance of a correlation is dependent on the number of values included in the calculation, or more precisely, the degrees of freedom. Fewer the number of values included in a correlation calculation, the greater the correlation coefficient must be in order for it to be significant. Little credence is given to correlation coefficients with only degrees of freedom (correlation coefficients with Be-Kd and Th-Kd), even if they are significant.

The significant correlation coefficients for the data presented in Table 8 have been printed in bold font. There were not many significant ($P < 0.05$) correlations between the various Kd values and the soil characteristics. The positive correlation coefficients of Ba-Kd, Mn-Kd, and Sr-Kd to >2-mm fraction is contrary to expectation and can not be explained. Generally, the greater the amount of large particles, the lower the surface area and therefore less sorption is expected. The positive correlation between Cu and organic C is well known and occurs because Cu forms an unusually strong complex to organic matter. Similar strong complexes with organic matter exist with Th and Ce, yet significant correlation coefficients were not calculated for this data set.

Table 8. Pearson Correlation Coefficients Between Desorption Kd Values (Table 7) and Physical Soil Properties (Table 4) ^(a) (excluded "greater than Kd values" from this Calculations.

	d.f. ^(a)	<2-mm	Sand	Silt	Clay	pH	Org. C	CEC	AEC	Fe-oxides
<2-mm	5.00	1.00								
Sand	5	-0.67	1.00							
Silt	5	0.12	-0.70	1.00						
Clay	5	-0.23	-0.38	0.21	1.00					
pH	5	-0.53	0.19	0.24	0.15	1.00				
Organic C	5	0.54	-0.35	-0.11	0.06	-0.97^(b)	1.00			
CEC	5	0.46	-0.86	0.92	0.11	0.14	-0.02	1.00		
AEC	5	0.21	-0.07	0.46	-0.76	0.03	-0.13	0.47	1.00	
Fe-oxides	5	0.40	-0.94	0.87	0.45	-0.05	0.24	0.89	0.13	1.00
Al-Kd	5	0.22	0.44	-0.71	-0.53	-0.71	0.56	-0.62	0.01	-0.57
Ba-Kd	5	0.99	-0.64	0.13	-0.28	-0.50	0.50	0.48	0.28	0.37
Be-Kd	2	0.86	-1.00	0.89	0.91	0.86	0.94	0.95	-0.49	1.00
Ce-Kd	4	0.15	-0.04	-0.22	0.00	-0.61	0.56	-0.25	-0.03	-0.11
Cr-Kd	5	0.02	0.53	-0.67	-0.45	-0.59	0.43	-0.64	0.02	-0.65
Cu-Kd	4	0.57	-0.48	-0.13	-0.13	-0.89	0.83	0.08	0.07	0.20
Fe-Kd	5	0.21	0.45	-0.76	-0.47	-0.68	0.54	-0.67	-0.09	-0.60
Mn-Kd	5	0.94	-0.75	0.11	0.08	-0.44	0.51	0.45	-0.09	0.49
Se-Kd	5	0.04	-0.66	0.65	0.67	0.55	-0.36	0.67	-0.21	0.71
Sr-Kd	5	0.95	-0.79	0.18	0.06	-0.43	0.50	0.52	-0.01	0.53
Th-Kd	2	0.52	0.08	-0.82	0.51	-1.00	0.98	-0.90	-0.57	-0.93
U238-Kd	4	-0.24	0.28	-0.12	0.08	-0.30	0.27	-0.37	-0.03	-0.24

^(a) Excluded "greater than Kd values" from calculations.

^(b) d.f. = degrees of freedom for variable. The degrees of freedom for the variables listed across the top of correlation matrix table are the same as those listed in this column.

^(c) In **Bold**: Correlation coefficients greater than 0.95, 0.88, 0.81 and 0.75, with 2, 3, 4, and 5 degrees of freedoms, respectively, are significant at $P < 0.05$ level (5% probability level).

3.3. Sorption Kd Values for Inorganic Contaminants

Sorption Kd values were measured for COCs for which there was not sufficient concentrations in the contaminated sediments to measure a desorption Kd value. Sorption Kd values were measured for Ba, Hg, K, Tc, and Tl. Barium Kd values were measured as an analog for radium Kd values. Kd values were measured using two initial contaminant spike

concentrations. Since the concentrations of the COCs at the study site are more similar to the lower spike concentrations, the lower concentration Kd values are more relevant to TNXOD OU conditions. The higher concentration was included to evaluate the linearity of the sorption isotherm, i.e., to evaluate whether the concentration of the contaminant influences Kd values. As can be seen in Table 9, initial concentrations greatly affect Ba and Hg Kd values, and have little effect on K, Tc, and Tl Kd values.

Measured sorption Hg values were quite high. These values are consistent with Hg-sorption Kd values measured with subsurface a sandy and a clayey sediment collected near the Ford Building Seepage Basin located on the SRS (Kaplan and Iversen 1999). Over a range of about 0.1 to 75 mg/L Hg(II), the Kd values for the sand ranged between ~1000 to ~2000 mL/g; the clay Kd values ranged from ~1000 to ~8000 mL/g. Unlike the TNXOD OU surface sediments used in this report, the subsurface Ford Building sediments contained very low concentrations of organic matter. This is important, in that high Hg-Kd values are commonly associated with sediments that have high organic matter.

The fact that some Tc sorption, albeit only small amounts, was measured is also noteworthy. In these sediments, the Tc sorption can likely be attributed to the presence of organic matter. The mechanism by which Tc sorbs to organic rich sediments has been attributed to the enhanced anion exchange capacity of such soils, and to the ability of the organic matter to reduce the Tc(VII) to the sparingly soluble Tc(IV) species. In this study, the more likely sorption mechanism appears to be anionic exchange because only 5 to 10% of the added Tc(VII) was removed from solution. Had the Tc(VII) been reduced, then one would expect that much more, perhaps all, of the Tc(VII) would be converted to Tc(IV), thereby leaving essentially no ⁹⁹Tc in the aqueous phase at the end of the sorption experiment.

Barium Kd values were measured by the sorption and desorption method. The desorption Kd values ranged from 326 to 6045 mL/g (Table 7). The sorption Kd values ranged from 67 to 347 mL/g (Table 9). The lower sorption Kd values are consistent with the notion that sorption Kd values do not account for the "aging" process between the contaminant and sediment.

Table 9. Adsorption Kd Values for Ba, Hg, K, Tc, and Tl

Element	Initial Conc. (µg/L)	Kd (mL/g)	Ave Kd (mL/g)	Stdev. Kd (mL/g)
Ba	643	374.14	347.04	26.94
		346.69		
		320.27		
	7637	73.46	67.30	5.36
		63.71		
64.73				
Hg	892	5581.88	5337.12	552.63
		4704.38		
		5725.09		
	12400	187.07	187.48	4.73
		192.40		
182.97				
K	1613	1.20	1.95	1.12
		1.42		
		3.24		
	14900	10.05	6.33	4.00
		8.99		
4.96				
Tc	1.5 µCi/L	1.31	4.65	6.83
		12.53		
		0.95		
	15 µCi/L	0.48	3.14	3.80
		3.60		
6.69				
Tl	942	-0.87	61.21	17.81
		67.15		
		41.19		
	9800	75.29	32.86	2.20
		32.88		
35.05				
		30.65		

3.4. Organic Contaminant Kd Estimates Based on K_{om}

Kd values for organic contaminants were calculated using an EPA-approved method (EPA 1996). The literature solubility values, octanol/water partition coefficients (K_{ow}), organic matter/water partition coefficients (K_{om}), and Kd values of the various organic compounds are presented in Tables 10 and 11. In general, the Kd values are ~ 0 mL/g. These are unexpectedly

low values considering the high organic matter concentrations in these sediments. This may in part be attributed to the assumption associated with Equation 6 that the only mechanism by which the organic compounds sorb to the sediment is by partitioning to the organic matter (driven by enthalpy) and that no sorption to the mineral phase occurs. This assumption becomes increasingly compromised as the hydrophobicity and the nonpolarity of the compound decreases. Although Equations 6 and 7 are commonly used to estimate organic compound K_d values, they may not be appropriate for these soils and contaminants, given the dominance of the mineral phase and the nonpolar character of the COCs. It is recommended that measured K_d values, instead of calculated K_d values for these contaminants be collected to verify these results.

Table 10. Kd Values for Organic Compounds in 6 Sediments Calculated from Organic Carbon Concentration and K_{ow} Data.

Compound	Solubility -log(mol/L)	log(Kow) (unitless)	Ref. ^a	log(Kom) From Equation 7	Kd (mL/g) ^b					
					Sediment 101	Sediment 102	Sediment 103	Sediment 104	Sediment 105	Sediment 106
cis-1,2-Dichloroethene	1.442	1.86	1	1.36	0.1	0.1	0.1	0.1	0.1	0.0
Trichloroethene	2.04	2.42	2	1.78	0.2	0.2	0.2	0.1	0.2	0.1
Carbon tetrachloride	2.2	2.73	2	1.89	0.2	0.2	0.2	0.2	0.2	0.2
Tetrachloroethene	3.04	2.88	2	2.48	0.8	0.9	0.9	0.7	0.9	0.6
Vinyl chloride	1.35	0.6	2	1.30	0.1	0.1	0.1	0.0	0.1	0.0

^a Reference for Solubility of K_{ow} values: 1 = Howard 1991; 2 = Schwarzenbach et al. 1992.

^b Fraction of organic matter in the sediment, f_{om} (kg om/kg sediment), for Sediment 101 = 0.0028, Sediment 102 = 0.0030, Sediment 103 = 0.0029, Sediment 104 = 0.0023, Sediment 105 = 0.0029, and Sediment 106 = 0.0020 (see Table 4).

Table 11. Statistical Description of the Organic Contaminant Kd Values Measured in Sediments 102, 103, 104, 105, and 106.

Compound	Median	Minimum	Maximum	Average	Std. Dev.
cis-1,2-Dichloroethene	0.1	0.0	0.1	0.1	0.0
Trichloroethene	0.2	0.1	0.2	0.2	0.0
Carbon tetrachloride	0.2	0.2	0.2	0.2	0.0
Tetrachloroethene	0.9	0.6	0.9	0.8	0.1
Vinyl chloride	0.1	0.0	0.1	0.1	0.0

3.5. Sequential Extractions

Sequential extractions (Table 2) were conducted on the six sediments collected from the TNXOD OU (Tables 1, 4, 5, and 6). Portions of the data generated from these extractions were used to calculate the desorption K_d values. Presented in Tables 12 and 13 are the percent concentrations of each COC. As mentioned in the Material and Methods section (Section 2), sequential extractions are designed to selectively recover certain fractions of the contaminant, depending on the fraction it is associated with (organic, amorphous Fe-oxide, crystalline Fe-oxide, or structural) or the process it is sorbed by (cation or anion exchange). Additionally, the sequence of the extractions generally becomes increasingly more vigorous.

There are a number of results from this work that can be used as supporting information for the selection of K_d values for the operable unit. A brief description of the overall trends observed in Tables 12 and 13, are (Exch = exchangeable, Org = organic, AmFeOx = amorphous Fe-oxide, CrFeOx = crystalline Fe-oxide, and Struct = structural):

- Ag and As were evenly distributed between the Org, AmFeOx, and CrFeOx fractions. Ag is a "soft metal" and therefore tends to partition to organic matter. As exists as an anion, thus it is not surprisingly associated with phases that are dominated by a large pH-dependent charge.
- Al was spread throughout, especially the Struct fraction. This was expected because Al exists in most minerals.
- Ba was found primarily in the exchangeable fraction. All elements in the IIA group in the periodic table (Be, Mg, Ca, Sr, Ba, and Ra) sorb primarily by cation exchange and surface complexation to Fe/Al oxides.
- Cd was associated primarily to Exch and Org fractions. These sites tend to sorb contaminants weakly.
- Ce was associated primarily to the Exch, Org, and Struct fractions.
- Cr was associated primarily to the Exch, Org, and AmFeOx fractions. These are the weaker sorbing sites. This is consistent with the notion that this contaminant exists primarily as an anion, CrO_4^- , and not as the sparingly soluble species Cr(III).
- Co was associated primarily with the Exch and Org sites.
- Cu was associated primarily with the Struct and CrFeOx fractions.
- Fe and Mn were found in most of the fractions. This is expected because these elements are found naturally in many minerals. Fe was especially abundant in the Org fraction, whereas Mn was found primarily in the Exch fraction.
- Ni was especially abundant in the Exch and Struct fractions.
- Pb was almost exclusively found in the Struct fraction.
- Sr was associated with the Exch and Struct fractions. This is consistent with the observation that naturally occurring Sr is abundant in groundwater and is known to be in the structure of many minerals.
- Hg was found almost exclusively in the Struct fraction. As the footnote to Table 13 indicates, AmFeOx and CrFeOx fractions could not be determined because the strong reducing agents used in the extraction solutions would convert $\text{Hg}^{2+}(\text{liq})$ into

Hg⁰(gas). The loss of Hg gas would result in an experimental artifact that is difficult to account for without expensive experimental protocols. Although AmFeOx is considered an "available phase," as defined in Equation 4, it is this researchers belief that the vast majority, if not all, of the Hg resided in a fraction that was very difficult to recover. Inconclusive evidence in support of this belief is the Hg analysis of the solid phase left after the first five extracts (extractions through to CrFeOx) had considerable amount of Hg still present, generally around 75% of the total Hg. Thus, if one was to assume that no volatilization occurred, which is unlikely, then >75% of the Hg was structural.

- **Tl** was associated primarily to the Org fraction. This is consistent with its "soft base" chemical properties.
- **Th**, which existed in very high concentrations in the contaminated sediments, was associated primarily with the Org and the AmFeOx fractions. This has important implications for remediation.
- **U** was associated with the Org and Exch fractions. This suggests that the U is not as strongly sorbed as many of the other contaminants, and that it will have a propensity to enter the mobile aqueous phase.

These results have important implications for remediation strategies. Assuming that the "exchangeable," "organic bound," and "amorphous Fe-oxide" fractions are more likely to enter the mobile aqueous phase or the biosphere, then Cd, Cr, Co, Tl, Th, and U are more likely to be remediated by phytoremediation or solvent extraction than Cu, Pb, and Hg. Conversely, Cu, Pb, and Hg would make better, albeit not the only, candidate contaminants for monitored natural attenuation than Cd, Cr, Co, Tl, Th, and U.

Table 12. Sequential Extraction Concentrations (%).

Sediment	Extractant	Ag	Al	As	Ba	Be	Cd	Ce	Cr	Co	Cu
101	Acid Extractable	3	27	0	52	(a)	0	44	24	69	4
	Organic Fraction	45	41	0	16		0	20	40	24	12
	Amorph. Fe-oxide	18	7	74	0		0	0	37	0	0
	Cryst. Fe-oxide	35	19	26	28		0	3	0	0	26
	Structural	0	6	0	4		0	33	0	7	58
102	Acid Extractable	0	14	0	68	100	28	25	10	64	1
	Organic Fraction	41	56	52	8	0	72	17	37	20	15
	Amorph. Fe-oxide	22	8	37	0	0	0	0	13	7	4
	Cryst. Fe-oxide	37	11	11	18	0	0	1	29	9	13
	Structural	0	11	0	6	0	0	56	11	0	67
103	Acid Extractable	0	5	0	34		0	14	8	79	14
	Organic Fraction	39	31	51	19		100	15	40	21	16
	Amorph. Fe-oxide	28	3	37	0		0	0	10	0	4
	Cryst. Fe-oxide	33	7	12	33		0	1	26	0	34
	Structural	0	53	0	14		0	70	15	0	32
104	Acid Extractable	0	7	13	48		0	12	7	68	8
	Organic Fraction	31	60	67	16		0	16	39	32	16
	Amorph. Fe-oxide	34	4	0	0		0	0	12	0	2
	Cryst. Fe-oxide	34	12	20	27		0	2	27	0	51
	Structural	0	17	0	9		0	70	15	0	23
105	Acid Extractable	0	8	0	60		100	27	16	72	8
	Organic Fraction	0	22	37	11		0	16	54	28	15
	Amorph. Fe-oxide	60	3	44	0		0	0	18	0	3
	Cryst. Fe-oxide	40	6	19	19		0	1	0	0	45
	Structural	0	61	0	9		0	56	12	0	29
106	Acid Extractable	0	17	0	52		0	30	12	0	4
	Organic Fraction	0	50	0	12		100	15	38	33	9
	Amorph. Fe-oxide	52	8	0	0		0	0	18	0	0
	Cryst. Fe-oxide	48	12	100	29		0	1	22	0	73
	Structural	0	12	0	7		0	54	10	67	14

(a) Empty Cells indicate that the constituent of concern was not detected in a particular fraction.

Table 13. Sequential Extraction Concentrations.

		Fe	Mn	Ni	Pb	Sr	Hg	Tl	Th-232	U-235	U-238
101	% Acid Extractable	2	76	33	0	68	0	5	0	0	0
	% Organic Fraction	61	7	16	0	1	0	38	61	0	9
	% Amorph. Fe-oxide	10	10	0	0	0	--	44	39	0	0
	% Cryst. Fe-oxide	23	6	51	0	3	--	13	0	0	0
	% Structural	4	1	0	0	28	100	0	0	0	91
102	% Acid Extractable	5	59	51	2	46	0	12	1	32	26
	% Organic Fraction	62	13	25	8	2	8	55	84	68	57
	% Amorph. Fe-oxide	19	10	0	3	0	--	0	10	0	4
	% Cryst. Fe-oxide	11	11	24	3	3	--	34	5	0	2
	% Structural	3	7	0	83	49	92	0	0	0	11
103	% Acid Extractable	6	15	54	1	43	0	0	1	44	36
	% Organic Fraction	49	2	23	8	2	100	62	65	51	37
	% Amorph. Fe-oxide	23	0	0	0	0	--	0	15	0	6
	% Cryst. Fe-oxide	20	0	23	2	3	--	38	7	5	3
	% Structural	3	83	0	89	52	0	0	12	0	17
104	% Acid Extractable	9	65	44	2	46	0	0	0	27	25
	% Organic Fraction	64	12	25	8	2	4	62	78	70	57
	% Amorph. Fe-oxide	8	0	0	0	0	--	0	6	0	3
	% Cryst. Fe-oxide	13	0	31	3	3	--	38	7	3	2
	% Structural	7	23	0	87	48	96	0	9	0	14
105	% Acid Extractable	3	57	40	5	45	0	0	1	29	26
	% Organic Fraction	54	20	24	7	1	0	0	88	71	56
	% Amorph. Fe-oxide	23	0	0	0	0	--	0	7	0	5
	% Cryst. Fe-oxide	15	0	36	2	2	--	100	4	0	2
	% Structural	5	23	0	86	51	100	0	0	0	12
106	% Acid Extractable	4	50	10	5	57	0	0	0	51	44
	% Organic Fraction	64	25	7	8	1	0	72	91	49	41
	% Amorph. Fe-oxide	17	17	0	0	0	--	0	7	0	3
	% Cryst. Fe-oxide	8	0	83	4	3	--	28	2	0	1
	% Structural	6	7	0	83	38	100	0	0	0	11

The amorphous Fe-oxide and the crystalline Fe-oxide fractions could not be determined for Hg because the strong reducing agent used in the extract would volatilize the Hg, thereby providing an experimental artifact. Thus the "Structural" fraction, in fact represent the sum of the "Amorphous Fe-oxide + Crystalline Fe-oxide + Structural" fractions.

3.6. Contaminant Association to Various Sediment Particle Sizes

The total COC concentrations of the whole sediment, $<2\text{-}\mu\text{m}$ fraction, and the $<0.5\text{-}\mu\text{m}$ fraction were determined. The intent of this work was to determine whether the COCs were enriched in the small size fractions and to evaluate whether it is likely that the contaminants were moving with mobile particulates, including colloids. Sediment 102 was the most contaminated sediment, with the highest concentrations of Cd, Ce, Co, Cr, Ni, and Sr. Sediment 102 is a surface sample collected closest to the point source (Table 1). Compared to the concentrations in the background sediment, Ag, Cr, Hg, Ni, Th-232, U-235 and U-238 concentrations were especially high in the sediments collected from the contaminated region of the TNXOD OU. There was little or no evidence of As, Ba, Be, Cd, Ce, Co, Cu, Mn, and Tl contamination in these sediments.

In Tables 14 and 15 the COC concentrations of the six sediments are presented. Those sediments collected from the contaminated region of the TNXOD OU that had COC concentrations in the whole sediment that were twice the concentration in the background sample, Sediment 101, were considered contaminated for this evaluation. The critical value of 2x the background concentration was selected arbitrarily. The sediments with 2x background concentration levels of a COC are identified in Tables 14 and 15 with bold font. Tables 14 and 15 also include the number of sediments in which the COC concentration in the whole sediment ($\text{COC}_{\text{whole}}$) was twice that measured in Sediment 101 ($\text{COC}_{\text{whole, Background}}$). COC enrichment was defined for this study as existing when the COC concentration in the $<0.5\text{-}\mu\text{m}$ fraction ($\text{COC}_{0.5\text{-}\mu\text{m}}$) was twice that measured in the whole sediment ($\text{COC}_{\text{whole}}$). COC exclusion was defined for this study as existing when the COC concentration of the whole sediments was twice that of the COC concentration in the $0.5\text{-}\mu\text{m}$ fraction. Based on these definitions, none of the COCs were enriched in $>50\%$ of the contaminated sediments (bold in Tables 14 and 15). Cadmium, Hg, and U-235 were excluded from $>50\%$ of the contaminated sediments. This latter finding indicates that Cd, Hg, and U-235 were primarily associated with the $>0.5\text{-}\mu\text{m}$ fraction (on a mass basis, as opposed to a volume or surface area basis).

These findings suggest that none of the COCs are moving primarily via particulate/colloid facilitated transport. Importantly, these findings do not rule out colloids as a possible vector. Instead they indicate, that if colloids are involved, they are not likely the only vector responsible for contaminant movement.

These findings also have important implications for remediation strategies. Based on Tables 14 and 15, soil washing, which is often designed to remove the smaller size fraction of contaminated sediments, is not a likely candidate for remediating these sediments. Soil washing is especially effective when a majority of the contaminants are associated with a small volume and well-defined size fraction of the total contaminated sediment. This was not consistently the case for any of the COCs measured in these sediments.

Table 14. Elemental Composition ($\mu\text{g/g}$) of the Whole, $<2\text{-}\mu\text{m}$, and $<0.5\text{-}\mu\text{m}$ Sediment Fraction and Comparison of COC Concentration in Whole Sediment versus in Background Sediment, Sediment 101

Sediment	Fraction	Ag	Al	As	Ba	Be	Cd	Ce	Cr	Co	Cu
101	Whole	<0.0001	1915	0.368	21.973	0.466	<0.00002	19.400	2.819	0.987	30.038
	$<2\text{ }\mu\text{m}$	2.610	11495	0.863	108.62	2.156	<0.00004	63.870	15.242	3.317	15.342
	$<0.5\text{ }\mu\text{m}$	3.602	10911	2.096	57.55	1.412	<0.0003	44.633	16.246	3.931	0.0001
102	Whole	1.803^(a)	6252	0.577	78.721	0.804	0.334	53.561	44.598	3.688	88.252
	$<2\text{ }\mu\text{m}$	<0.0002	11427	1.057	85.842	1.154	<0.00006	54.590	46.876	4.042	21.199
	$<0.5\text{ }\mu\text{m}$	2.814	8070	2.006	53.123	0.770	<0.0002	41.754	39.138	3.043	<0.0001
103	Whole	<0.0001	2828	0.289	16.371	0.198	<0.00002	11.278	30.654	1.225	48.478
	$<2\text{ }\mu\text{m}$	2.304	5893	1.059	36.026	0.469	0.1101	19.177	102.04	1.236	14.965
	$<0.5\text{ }\mu\text{m}$	0.9411	4990	1.565	24.403	0.355	0.0691	15.200	309.92	2.193	<0.0001
104	Whole	0.729	2338	0.439	17.326	0.228	0.0139	10.338	66.264	0.876	57.986
	$<2\text{ }\mu\text{m}$	1.306	6788	0.955	25.187	0.290	<0.00004	20.823	95.319	1.175	17.014
	$<0.5\text{ }\mu\text{m}$	0.739	5644	1.415	17.811	0.216	<0.00006	15.970	69.664	0.796	<0.0001
105	Whole	0.258	3371	0.508	15.821	0.154	0.0496	15.042	78.158	1.080	55.155
	$<2\text{ }\mu\text{m}$	1.144	9799	0.679	40.086	0.793	0.0905	35.992	34.937	1.420	9.547
	$<0.5\text{ }\mu\text{m}$	0.888	10585	1.214	39.995	0.780	<0.00008	35.355	34.558	1.422	0.0001
106	Whole	0.3433	4847	0.398	28.616	0.522	0.0531	32.854	25.909	1.018	57.450
	$<2\text{ }\mu\text{m}$	<0.0001	11781	0.639	50.418	0.677	<0.00003	24.658	87.214	2.928	10.782
	$<0.5\text{ }\mu\text{m}$	<0.0002	11917	1.110	45.254	0.625	<0.00007	22.363	79.192	2.811	52.582

Number of sediments with $\text{COC}_{\text{Whole}}$ is $>2\times \text{COC}_{\text{Whole, Background}}$	4	2	0	1	0	3	1	5	1	1
Number of sediments with enrichment ($\text{COC}_{0.5\text{-}\mu\text{m}}$ is $>2\times \text{COC}_{\text{Whole}}$)	1	1	0	0	0	0	0	2	0	0
Number of sediments with exclusion ($\text{COC}_{\text{Whole}}$ is $>2\times \text{COC}_{0.5\text{-}\mu\text{m}}$)	0	0	0	0	0	3	0	1	0	1
Number of sediments with no enrichment or exclusion	3	1	0	1	0	0	1	2	1	0

^(a) Bold identify sediments with $\text{COC}_{\text{Whole}}$ is $>2\times \text{COC}_{\text{Whole, sediment 101}}$; Sediment #101 is an uncontaminated sediment.

Table 15. Elemental Composition ($\mu\text{g/g}$) of the Whole, $<2\text{-}\mu\text{m}$, and $<0.5\text{-}\mu\text{m}$ Sediment Fraction and Comparison of COC Concentration in Whole Sediment versus in Background Sediment, Sediment 101.

Sediment	Fraction	Fe	Hg	Mn	Ni	Pb	Sr	Tl	Th 232	U-235	U-238
101	Whole	2635	0.034	84.28	1.869	4.093	1.464	0.117	2.709	<0.00002	0.573
	$<2\text{ }\mu\text{m}$	14622	0.171	204.05	4.215	15.517	4.513	0.783	6.329	<0.00002	1.830
	$<0.5\text{ }\mu\text{m}$	12288	0.303	94.36	0.000	18.977	2.191	1.345	24.686	<0.00002	1.979
102	Whole	7533^(a)	6.821	114.37	18.823	17.605	7.158	0.075	201.005	1.196	187.663
	$<2\text{ }\mu\text{m}$	11390	1.686	137.88	17.729	36.930	4.438	0.000	224.478	0.914	147.112
	$<0.5\text{ }\mu\text{m}$	9295	0.983	71.64	12.599	20.673	2.532	2.570	207.226	<0.00002	127.713
103	Whole	1798	0.524	25.11	4.877	0.000	3.198	0.079	49.477	2.127	285.107
	$<2\text{ }\mu\text{m}$	12287	10.420	36.39	11.085	19.436	7.617	1.138	1452.734	2.426	427.905
	$<0.5\text{ }\mu\text{m}$	11365	5.626	35.21	162.929	17.277	4.710	1.368	1186.638	1.936	351.890
104	Whole	5490	9.454	20.84	9.781	10.459	3.608	0.087	694.863	1.808	329.144
	$<2\text{ }\mu\text{m}$	6383	6.759	27.62	6.858	18.868	2.379	0.771	849.770	4.540	640.345
	$<0.5\text{ }\mu\text{m}$	5555	5.747	16.28	4.951	16.535	1.683	1.017	802.642	3.447	503.490
105	Whole	3885	9.203	22.18	6.779	13.566	1.309	0.000	390.063	4.023	559.268
	$<2\text{ }\mu\text{m}$	6898	0.396	21.91	11.789	29.799	2.237	0.633	63.809	1.524	261.503
	$<0.5\text{ }\mu\text{m}$	7111	0.442	17.59	13.453	35.615	1.826	1.125	75.697	1.567	279.734
106	Whole	3794	0.636	13.52	13.098	24.896	2.588	0.133	29.169	1.583	287.712
	$<2\text{ }\mu\text{m}$	5847	0.848	52.85	11.694	21.530	6.447	0.000	164.818	4.796	646.347
	$<0.5\text{ }\mu\text{m}$	5397	0.745	45.66	14.265	21.379	4.268	0.000	158.384	4.722	633.242
Number of sediments where $\text{COC}_{\text{Whole}}$ is $>2\times \text{COC}_{\text{Whole, Background}}$		2	4	0	5	4	3	0	5	5	5
Number of sediments where enrichment ($\text{COC}_{0.5\text{-}\mu\text{m}}$ is $>2\times \text{COC}_{\text{Whole}}$)		0	1	0	1	1	1	0	2	1	1
Number of sediments where exclusion ($\text{COC}_{\text{Whole}}$ is $>2\times \text{COC}_{0.5\text{-}\mu\text{m}}$)		0	2	0	0	0	1	0	1	3	1
Number of sediments with no enrichment or exclusion		2	1	0	4	3	1	0	2	1	3

^(a) Bold identify sediments where $\text{COC}_{\text{Whole}}$ is $>2\times \text{COC}_{\text{Whole, sediment 101}}$; Sediment #101 is an uncontaminated sediment.

4. Conclusions

Kd values for constituents of concern (COCs) for the TNX Outfall Delta Operable Unit (TNXOD OU) were measured and calculated in this study. Kd values for inorganic COCs were measured using two techniques: desorption and (ad)sorption techniques. Kd values for organic COCs were calculated from an EPA-approved method based on the solubility of the COC and the concentration of organic matter in the sediment. Additionally, Kd values for some COCs were estimated, based on geochemical analogies. Geochemical analogies were necessary when various COCs were below detection limit in the contaminated sediments and were not included in the sorption-Kd tests. Ce-Kd values measured were used to estimate the Ac, Cm, and Pm Kd values. These elements have similar geochemical (Kaplan and Serne 1999, Thibault et al. 1990) and chemical properties, including +3 oxidation states and large atomic weights. Desorption Kd values for Ca were used to estimate Be-Kd values. Be existed in below detection limits in the five contaminated sediments. Ca is in the same period group as Be, Group IIA. Calcium would be expected to sorb slightly more strongly than Be. Consequently, the Be-Kd estimates were very conservatively set to half the measured Ca values. Finally, measured desorption Ba-Kd values were used to estimate Ra Kd values. Ba exists just above Ra in the IIA Group in the periodic table, and it is expected to sorb slightly less strongly to sediments than Ra. Hence, Ba would be expected to provide a conservative estimate of Ra sorption.

Reasonably Conservative and Upper Limit Kd values for each of the COCs are presented in Table 16. The sources of these data are also provided in the table. Reasonably Conservative values were the lowest measured or calculated (for organic COCs) Kd values, whereas the Upper Limit values were the highest measured or calculated Kd values. In general, most of the in-situ Kd values were appreciably larger than default conservative Kd values used in previous contaminant transport calculations. In the case of the desorption experiments, the cause for the large values can in part be attributed to the contaminants having several years to "age" with the sediments. During the aging process, the sorbed contaminants may be incorporated into the structure of the solid phase or be buried on the solid phase beneath recently formed precipitates (e.g., Fe-oxide or carbonate coatings), thereby limiting re-entry into the mobile aqueous phase. The organic-COC Kd values were generally quite low. This may be attributed to the implicit assumption associated with the calculation that sorption occurs only by partitioning to the organic matter (driven primarily by enthalpy) and not to the mineral phase. This assumption is increasingly inaccurate as the hydrophobicity of organic solute and the proportion of mineral surfaces increases.

The sequential extraction experiment revealed that Cu, Hg, and Pb were strongly bound onto the sediment, providing supporting evidence for selecting large Kd values for these COCs. Conversely, Cd, Cr, Co, and Tl, tended to be associated with the "exchangeable" and "organically bound" fractions, providing supporting evidence for selecting lower Kd values for these COCs. Measurements were conducted of the COC concentrations in the whole sediment, the <2- μ m fraction, and the <0.5- μ m fractions. The motivation behind these measurements was to test the hypothesis that some of the less soluble COCs, such as Th and Hg, may have been

transported at the study site via mobile colloids. Among the most contaminated sediments, there was only sporadic evidence of contaminant-concentration enrichment in the smaller fractions. These data do not rule out the possibility that COCs may be moving via colloid transport, but do strongly suggest that colloids are not the only means for COC transport.

The sequential extraction and the COC concentration versus size fraction data have important implications for remediation strategies. Assuming that the "exchangeable," "organic bound," and "amorphous Fe-oxide" fractions are more likely to enter the mobile aqueous phase or the biosphere, then Cd, Cr, Co, Tl, Th, and U are more likely to be remediated by phytoremediation or solvent extraction than Cu, Pb, and Hg. Conversely, Cu, Pb, and Hg would make better candidate contaminants for monitored natural attenuation than Cd, Cr, Co, Tl, Th, and U. The COC versus size fraction data suggests that soil washing, which removes the smaller size fraction of contaminated sediments, would not be an effective strategy for remediating these sediments. Soil washing is especially effective when a majority of the contaminants are associated with a small volume of sediment existing in a narrow particle size range. This was not consistently the case for any of the COCs measured in this study.

In summary, this study provided technically defensible evidence for selecting several Kd values, especially for the inorganic COCs, which are appreciably greater than present literature-derived values. These site-specific values will improve accuracy and remove some unnecessary conservatism in future transport and risk calculations associated with the TNX Outfall Delta Operable Unit.

Table 16. Reasonably Conservative and Upper-Limit Kd Values (mL/g) Based on Values Measured or Calculated in this Study.

	Reasonably Conservative	Upper- Limit	Data Source
Ac	255	4074	Based on Desorption Test, using Ce as an analog
Ag	>233	>1947	Desorption Test
Al	228	1930	Desorption Test
As	55	592	Desorption Test
Ba	320	374	Adsorption Batch Test
Be	45	181	Based on Desorption Test, using Ca as an analog
Cd	39	39	Desorption Test
Ce	255	4074	Desorption Test
Cm	255	4074	Based on Desorption Test, using Ce as an analog
Cr	58	2062	Desorption Test
Cu	67	290	Desorption Test
Fe	199	2589	Desorption Test
Hg	4704	5725	Adsorption Batch Test
K	1.2	3.2	Adsorption Batch Test
Mn	268	3108	Desorption Test
Ni	257	404	Desorption Test
Pb	>11460	>38751	Desorption Test
Pm	255	4074	Based on Desorption Test, using Ce as an analog
Ra	336	393	Based on Adsorption Test, using Ba as an analog
Se	219	267	Desorption Test
Sr	1676	5518	Desorption Test
Tc	0.5	12.5	Adsorption Batch Test
Tl	41	75	Adsorption Batch Test
Th	115	2255	Desorption Test
U	170	6493	Desorption Test
cis-1,2-Dichloroethene	0	0.1	Calculated from Literature Kow/Solubility Values
Trichloroethene	0.1	0.2	Calculated from Literature Kow/Solubility Values
Carbon Tetrachloride	0.2	0.2	Calculated from Literature Kow/Solubility Values
Tetrachloroethene	0.6	0.9	Calculated from Literature Kow/Solubility Values
Vinyl Chloride	0	0.1	Calculated from Literature Kow/Solubility Values

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7. Appendix A: Detailed Sequential Extraction Procedure

Materials

Five contaminated and one uncontaminated (background:101, BG5-0) sediment from the TNX OD were used in this study (Table A1). These sediments were selected because it was anticipated that they would have high contaminant concentrations based on contamination maps previously reported. The sediments were collected by a private contractor and delivered to our laboratory through standard Chain of Custody protocol.

Table A1. Sediment identification and description.

Chain of Custody ID#	Chain of Custody Description	Sample Depth (ft)	Expt. ID#, Description
119329	TNXOD-BG5K	0.4 to 1.4	101, BG5-0
119312	TNXOD-A5K	0 to 1	102, A5-0
119316	TNXOD-B5K	0.5 to 1	103, B5-0.5
119321	TNXOD-C5K	1 to 2	104, C5-1
119322	TNXOD-D28K	0 to 1	105, D28-0
119325	TNXOD-B3K	0.2 to 0.5	106, B3-0

- Uncontaminated surface water was collected from TNX wetland, north of the contaminated TNXOD OU.
- Acid Soluble Extract: 0.44 M CH_3COOH + 0.1 M $\text{Ca}(\text{NO}_3)_2$. Weighed out 11.07 g $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 12.6 mL of Glacial acetic acid into a 500 mL volumetric and diluted with Milli-Q water
- Organically Bound Extract: 0.1 M $\text{Na}_4\text{P}_2\text{O}_7$. Weighed out 22.0302 g of $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ into a 500-mL volumetric flask and diluted with Milli-Q water.
- Amorphous Fe-Oxide Extract (acidified ammonium oxalate, pH 3.): Prepared a solution of 0.175 M ammonium oxalate $[(\text{NH}_4)_2\text{C}_2\text{O}_4 + 0.1\text{-M oxalic acid } (\text{H}_2\text{C}_2\text{O}_4)]$. Weighed out 12.435 g of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and 6.305 g of $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ into ~400 mL deionized water, adjusted to pH 3.0 by adding NH_4OH or HCl , and diluted to 0.5 L final volume.
- Crystalline Fe-oxide Extract (Citrate buffer; 0.15 M Na-citrate + 0.05 M Citric acid): Bring 22.06 g Na citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$) and 5.25 g citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) up to 500 mL with H_2O .
- Aqua Regia: 1 part HNO_3 : 3 parts HCl plus 1 part water.

Saturated Paste Extracts

1. Gravimetrically determined the moisture content of the sediments.

In triplicate, added ~10-g of sediment to tared aluminum weighing boats.

Left in hood to air-dry until weights did not change.

Calculate % Air-dry weight as: $\% \text{ Air-dry weight} = (1 - [(W_i - W_f)/W_i]) * 100$.

2. Made a saturated paste using the procedure of Rhoades (1996).

Added 600-mL of field moist sediment into a tared, 1-L glass beaker.

3. Weighed moist sediment and beaker.
4. Added $<0.45\text{-}\mu\text{m}$ filtered TNX surface water while stirring until sediment was nearly saturated.
5. Allowed the mixture to stand covered for several hours.
6. The criteria for a saturated paste were as follows:
 - glistened as it reflects light,
 - flowed slightly when the container is tipped,
 - slid freely and cleanly off a smooth spatula, and
 - consolidated easily by tapping or jarring the container after a trench is formed in the paste.
7. Upon attainment of saturation, weighed the container plus contents.
8. Covered samples with parafilm and let sample stand for 7 additional days.
9. Transferred paste to a filter funnel fitted with a filter paper. Filtered and saved filtrate and solids for subsequent analyses.
10. Refiltered through a $0.45\text{-}\mu\text{m}$ filter. Saved filtrate for subsequent chemical characterization.

Acid Soluble Extraction

1. The following extractions were conducted in duplicate. For each sediment, weighed 1.0-g dry weight into tared, 35-mL centrifuge tubes. Recorded actual weight of "Tare + sed. dry wt. at start of acid soluble fraction."
2. Added 30-mL acid-soluble extraction solution to each tube.
3. Weighed sample and recorded "Tare + wet sed. + extract wt. for acid soluble fraction."
4. Placed on shaker for 1 day.
5. Centrifuged for 20 min at 6000 rpm.
6. Recovered supernate.
7. Pass supernate through a $0.45\text{-}\mu\text{m}$ filter. Saved filtrate for subsequent chemical characterization.
8. Added 20 mL of $0.0125\text{ Ca(NO}_3)_2$ wash solution to each tube.
9. Mixed by hand for 1 min.
10. Centrifuged for 20 min at 6000 rpm.
11. Discarded aqueous.

Organic Extraction

1. The following extractions were conducted in duplicate. Recorded weight of "tube and sed. wet weight for organic fraction."
2. Added 30 mL organically bound extractant to each tube.
3. Weighed sample and recorded "Tare + wet sed. + extract wt. for organic bound fraction."
4. Placed on shaker for 1 day.
5. Centrifuged for 20 min at 6000 rpm.
6. Recovered supernate.

7. Pass supernate through a 0.45- μ m filter. Save this solution for subsequent chemical characterization.
8. Added 20 mL of 0.0125 $\text{Ca}(\text{NO}_3)_2$ wash solution to each tube.
9. Mixed by hand for 1 min.
10. Centrifuge for 20 min at 6000 rpm.
11. Discarded aqueous.

Amorphous Fe-Oxide Extraction

1. The following extractions were conducted in duplicate. Wrapped each tube in aluminum foil to avoid exposure to light. Recorded weight of "tube and sed. wet wt. for Amorphous Fe-Oxide fraction."
 2. Added 30-mL Amorphous Fe-Oxide Extract to each tube. Minimized amount of light that came into contact with the suspensions by keeping the lights low, the samples in aluminum foil, and the samples in opaque boxes.
 3. Weighed sample and recorded "Tare + wet sed. + extract wt. for amorphous Fe-oxide fraction."
 4. Placed on shaker for 30 min.
 5. Centrifuge for 20 min at 6000 rpm.
 6. Recovered supernate.
- Pass supernate through a 0.45- μ m filter. Save solution for subsequent chemical characterization.
8. Added 20 mL of 0.0125 $\text{Ca}(\text{NO}_3)_2$ wash solution to each tube.
 9. Mixed by hand for 1 min.
 10. Centrifuged for 20 min at 6000 rpm
 11. Discarded aqueous.

Crystalline Fe-oxide Extraction

1. Record weight of "tube and sed. wet weight for Crystalline. Fe-oxide" in Table A2.
2. Add 15-mL citrate buffer to each tube.
3. Add 0.75-g sodium dithionite (or sodium hydrosulfite, $\text{Na}_2\text{S}_2\text{O}_4$, F.W. = 174.1) to each test tube.
4. Shake by hand for 15 sec.
5. Weigh sample and record "Tare + wet sed. + extract wt. for Crystalline Fe-oxide fraction."
6. Put in water bath shaker for 30 min at 50°C. Dry tubes when done.
7. Centrifuge for 10 min at 6000 rpm.
8. Recover supernate.
9. Pass through a 0.45- μ m filter.
10. Add 75- μ L of Ultrex (or Ultra Pure) HNO_3 to each tube to preserve sample for analyses.
11. Add 20 mL of 0.0125 $\text{Ca}(\text{NO}_3)_2$ wash solution to each tube.
12. Mix by hand for 1 min.
13. Centrifuge for 10 min at 6000 rpm
14. Remove liquid and throw away.

15. Send solids 101, 104, 107, 110, 113, and 116 to Chuck Coleman for rad disc microwave digestion.

Table A2. Weights used in crystalline Fe-oxide fraction.

ID#	Sediment Description	Rep	Centrifuge tare wt. (g)	Tare + sed. wet wt. at start of cryst. Fe-oxide fraction (g)	Tare + wet sed. + extract wt. for cryst. Fe-oxide fraction (g)
501	101, BG5-0.4	1			
502		2			
503		3			
504	102, A5-0	1			
505		2			
506		3			
507	103, B5-0.5	1			
508		2			
509		3			
510	104, C5-1	1			
511		2			
512		3			
513	105, D28-0	1			
514		2			
515		3			
516	105, B3-0.2	1			
517		2			
518		3			

Residual and Total Digestion

1. Label and weigh aluminum weighing boats (1 for each tube).
2. Squirt di-water into the centrifuge tubes generated from Crystalline Fe-oxide Extraction to loosen and flush out the pellet into the aluminum boat.
3. Dry at 105°C until constant weight.
4. Add 0.2 to 0.3 g of dry residue to each Parr Bomb teflon containers (1 per sample).
5. Add 1 mL Aqua regia + 10 mL 48% hydrofluoric acid to each vessel.
6. Place containers into Parr Bomb cases and the Parr Bombs cases into an oven at 110°C for 3 hours.
7. Remove Parr Bombs from oven. Let cool to room temperature.
8. Pass through 0.45- μ m filter. Bring filtrate up to volume with di-water in a 25-ml volumetric flask.
9. Send out for analysis.

Chemical Analysis

Chemical analyses were conducted by the Analytical Development Section (ADS), Measurement Technology Department, Savannah River Technology Center. Table A3 contains the types of analyses performed on each sample.

Table A3. Samples to be submitted to ADS for chemical analyses.

#	Sediment	Extract	Solid/Liquid	Analyses
1	101	Water	Liquid	ICP-AES, ICP-MS, Hg, Se
2	102		Liquid	ICP-AES, ICP-MS, Hg, Se
3	103		Liquid	ICP-AES, ICP-MS, Hg, Se
4	104		Liquid	ICP-AES, ICP-MS, Hg, Se
5	105		Liquid	ICP-AES, ICP-MS, Hg, Se
6	106		Liquid	ICP-AES, ICP-MS, Hg, Se
7	101	Acid	Liquid	ICP-AES, ICP-MS, Hg, Se
8	102		Liquid	ICP-AES, ICP-MS, Hg, Se
9	103		Liquid	ICP-AES, ICP-MS, Hg, Se
10	104		Liquid	ICP-AES, ICP-MS, Hg, Se
11	105		Liquid	ICP-AES, ICP-MS, Hg, Se
12	106		Liquid	ICP-AES, ICP-MS, Hg, Se
13	101	Organic	Liquid	ICP-AES, ICP-MS, Hg, Se
14	102		Liquid	ICP-AES, ICP-MS, Hg, Se
15	103		Liquid	ICP-AES, ICP-MS, Hg, Se
16	104		Liquid	ICP-AES, ICP-MS, Hg, Se
17	105		Liquid	ICP-AES, ICP-MS, Hg, Se
18	106		Liquid	ICP-AES, ICP-MS, Hg, Se
19	101	Amorphous Fe-oxide	Liquid	ICP-AES, ICP-MS, Hg, Se
20	102		Liquid	ICP-AES, ICP-MS, Hg, Se
21	103		Liquid	ICP-AES, ICP-MS, Hg, Se
22	104		Liquid	ICP-AES, ICP-MS, Hg, Se
23	105		Liquid	ICP-AES, ICP-MS, Hg, Se
24	106		Liquid	ICP-AES, ICP-MS, Hg, Se
25	101	None	Solid	Organic Carbon
26	102		Solid	Organic Carbon
27	103		Solid	Organic Carbon
28	104		Solid	Organic Carbon
29	105		Solid	Organic Carbon
30	106		Solid	Organic Carbon

8. Appendix B: Detailed Sorption Kd Procedure

The sorption Kd method is based on ASTM D 4319 [ASTM 1984]). Sample preservation followed EPA 245.1 Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry revision 3.0 5/94. Sample analyses were conducted by the General Engineering Laboratories (Charleston, SC), who followed EPA SW-846 Method 6010B by ICP and EPA SW-846 Method 7470A by CVAA (Cold Vapor Atomic Absorption).

Materials

- 0.02 M NaNO₃ (pH 5.1)
- Sediment TNXOD-BG5K, collected from an uncontaminated area of TNX near the Outfall Delta, depth of sample was 0.4 to 1.4 ft
- Uncontaminated TNX surface water (<0.45-μm filter)
- 1 mg/L Tl (from TlCl) in uncontaminated TNX surface water
- 10 mg/L Tl (from TlCl) in uncontaminated TNX surface water
- 0.2 ppm Hg (from mercury II nitrate monohydrate, Aldrich; also 1e-6 M Hg) in uncontaminated TNX surface water. This was prepared using a 400 mg/L Hg stock solution that was prepared by dissolving 34.16 mg Hg(NO₃)₂·H₂O into 0.05-L 0.1 M HNO₃. Then 0.125 mL of the 400 mg/L Hg stock solution was brought up to 250 mL with TNX surface water (<0.45-μm, pH 5.1).
- 2 ppm Hg (from mercury II nitrate monohydrate, Aldrich; also 1e-5 M Hg) in uncontaminated TNX surface water. This was prepared using a 400 mg/L Hg stock solution that was prepared by dissolving 34.16 mg Hg(NO₃)₂·H₂O into 0.05-L 0.1 M HNO₃. Then 2.507 mL of the 400 mg/L Hg stock solution was brought up to 250 mL with uncontaminated TNX surface water (<0.45-μm, pH 5.1).
- 1 mg/L K (from KCl) in 0.02 M NaNO₃ (pH 5.1)
- 10 mg/L K (from KCl) in 0.02 M NaNO₃ (pH 5.1).
- 1.5 μCi/L ⁹⁹Tc (from ⁹⁹TcO₄⁻ carrier-free source) in Uncontaminated TNX surface water
- 15-μCi/L ⁹⁹Tc (from ⁹⁹TcO₄⁻ carrier-free source) in Uncontaminated TNX surface water
- 1 mg/L Ba (from BaCl₂) in Uncontaminated TNX surface water
- 10 mg/L Ba (from BaCl₂) in Uncontaminated TNX surface water
- Nitric Acid (1+1): Prepare this in non-rad hood. Add 500 mL concentrated Ultrex or UltraPure HNO₃ to 400 mL of d.i. water and dilute to 1 L.

Methods

1. Following the treatment description presented in Table B1, add 0.35-g sediment to tared Oak Ridge Tubes. Record "tare + sed dry wt."
2. Preequilibrate the sediments with 3 2-hr washes with 0.02 M NaNO₃ (pH 5.1) for the K-Kd tests and uncontaminated TNX surface water for all other Kd tests. At the end of each wash, centrifuge at ~13000 g's for 10 min. Throw away the wash solutions being very careful not to lose any sediment. Error on the side of leaving liquid in the tube, rather than losing solids. Record "tare + wet soil wt" after the third wash.

3. Add 35 mL of the appropriate solution. Record "tare + wet soil + soln wt."
4. Put on shaker for 1 week.
5. Centrifuge and pass aqueous through 0.45- μ m filter.
6. Preserve aqueous sample by adding 3 mL Nitric Acid (1+1) /L sample [e.g., if you have 32 mL of filtrate sample, add 0.96 mL Nitric Acid (1+1)].
7. Save aqueous and analyze as follows
 - K by AA flame
 - Hg by AA-hydride generation
 - Ba and Tc by ICP-ES
 - Tc-99 by total nonvolatile beta (since the sample contained no other beta emitters, only Tc-99 contributed to the total nonvolatile beta activity.)
 - Do complete cation (ICP-ms), anion (IC), total alkalinity (titration), and total organic and inorganic carbon (TIC and TOC) analyses of the uncontaminated surface water used in these experiments.

Table B1. Experimental Treatment Factorial

ID #	Element	Target spike Concentration (ppm)	Sediment Present
601-603	Hg	0.2	Present
604-606			Not Present
607-609		2	Present
610-612			Not Present
613-615	K	1	Present
616-618			Not Present
619-621		10	Present
622-624			Not Present
625-627	Tl	1	Present
628-630			Not Present
631-633		10	Present
634-636			Not Present
637-639	Tc	1.5 μ Ci/L	Present
640-642			Not Present
643-645		15 μ Ci/L	Present
646-648			Not Present
649-651	Ba	1	Present
652-654			Not Present
655-657		10	Present
658-660			Not Present

9. Appendix C: Supplemental Data

Appendix C1. ICP-ES and AA Results (mg/L) from Desorption Kd Tests

Sed	Extract	Ag	Al	Ba	Be	Ce	Cr	Cu	Fe	Mn	Ni	Pb	Sr	Tl	Se
101	water	0.04	0.418	0.173	0.001	0.315	0.009	0.006	0.122	3.337	0.021	0.029	0.075	0.328	0.00625
102	water	0.004	3.304	0.015	0.001	0.315	0.036	0.066	3.484	0.038	0.03	0.029	0.015	0.134	0.0067
103	water	0.004	4.909	0.019	0.001	0.315	0.113	0.069	6.265	0.016	0.021	0.029	0.025	0.134	0.007
104	water	0.04	17.432	0.066	0.01	3.15	0.946	0.177	20.736	0.07	0.13	0.29	0.047	1.341	0.00725
105	water	0.004	7.121	0.038	0.001	0.315	0.021	0.029	4.639	0.037	0.013	0.029	0.04	0.207	0.0109
106	water	0.004	11.891	0.035	0.001	0.315	0.041	0.029	3.32	0.081	0.013	0.029	0.041	0.19	0.0101
101	acid	0	16.42	0.424	0	0	0.167	0	0.436	2.164	0	0	2.028	105.96	0.00145
102	acid	0	42.314	2.906	0.016	0	0.314	0.281	19.024	3.047	0.277	0	2.265	99.933	0.0024
103	acid	0	18.551	0.497	0	0	0.338	0.179	21.781	0.853	0.279	0	2.132	95.629	0.0032
104	acid	0	15.819	0.583	0	0	0.248	0.134	16.604	0.701	0.134	0	2.066	93.907	0.004
105	acid	0	41.265	1.106	0	0	0.258	0.114	4.879	0.241	0	0	2.158	95.629	0.00475
106	acid	0	19.737	0.481	0	0	0.275	0	2.425	0.457	0	0	2.144	105.1	0.0053
101	organic	0.073	24.668	0.125	0	0	0.275	0	15.241	0.202	0	0	0.528	0	0.02442
102	organic	0.047	154.32	0.334	0	0	1.104	0.384	220.58	0.619	0	0	0.671	0	0.0429
103	organic	0.086	102.33	0.259	0	0	1.559	0.194	180.35	0.134	0	0.547	0.721	0	0.05016
104	organic	0.1	135.15	0.182	0	0	1.255	0.277	110.37	0.119	0.135	0.538	0.728	0	0.05346
105	organic	0.042	111.57	0.197	0	0	0.831	0.174	84.598	0.08	0	0.293	0.676	0	0.06402
106	organic	0	57.256	0.108	0	0	0.813	0.079	38.111	0.224	0	0	0.377	0	0.06798
101	AmFeOx	0	4.138	0	0	0	0.247	0	2.43	0.274	0	0	0	0	0.00.6
102	AmFeOx	0	21.6	0	0	0	0.391	0	65.908	0.499	0	0	0	9.356	0.00456
103	AmFeOx	0	9.335	0	0	0	0.367	0	77.323	0	0	0	0	0	0.0048
104	AmFeOx	0.211	9.165	0	0	0	0.367	0	13.207	0	0	0	0	8.055	0.00504
105	AmFeOx	0	15.8	0	0	0	0.256	0	34.23	0	0	0	0	8.922	0.0054
106	AmFeOx	0.236	8.824	0	0	0	0.364	0	9.778	0.146	0	0	0	7.621	0.00582

Comments:

- To facilitate spreadsheet calculations of Kd values, zero's were entered in "below-detection limit" values.
- For the Acid, Organic, and Amorphous Fe-oxide extracts, 0 mg/L were entered into spreadsheet so that these values could be included in summation to generate the C_{solid} values used in the Kd_{max} calculations.
- Tl values determined by ICP-ES are suspect because they are unrealistically high and essentially no Tl was detected by ICP-MS. Based on conversations with the spectroscopist, the Tl is likely the result of spectral interferences.

Appendix C2. ICP-MS Analytical Results (µg/L) for Desorption Kd Tests.

ID	Extract	Co	Ni	Cu	Zn	As	Sr	Ag	Cd	Ce	Tl	Pb	Th	U
101	water	0.06	0.15	0.18	0.82	0.06	76.75	159.67	0.01	0.01	0.00	0.21	0	0
102	water	0.06	18268.68	76.10	0.82	0.06	15.66	75.63	29.96	21.54	0.00	0.21	0	120.44
103	water	0.06	0.15	82.14	0.82	6.50	26.81	59.60	0.01	7.00	0.00	0.21	390.74	253.30
104	water	0.06	0.15	196.00	0.82	35.85	48.36	31.15	0.01	58.22	0.00	0.21	1779.43	3054.05
105	water	0.06	0.15	32.45	0.82	0.06	42.47	28.34	0.01	7.23	0.00	0.21	26.01	39.74
106	water	0.06	0.15	27.17	0.82	0.06	42.99	15.80	0.01	6.45	0.00	0.21		126.83
101	acid	22.19	95.68	40.94	0	0	2288.01	144.29	0	209.51	0	0	0	0
102	acid	97.59	445.29	32.03	0	0	2435.88	0	11.79	1012.63	0	53.42	43.59	1605.89
103	acid	50.27	466.05	229.42	0	0	2319.13	0	0	169.53	0	17.48	365.18	4941.60
104	acid	32.90	260.40	171.00	0	11.89	2279.87	0	0	236.17	0	64.36	23.36	5422.42
105	acid	33.46	261.22	152.43	0	0	2359.11	0	5.04	614.49	0	111.43	12.01	2517.09
106	acid	0	164.28	80.80	0	0	2302.32	0	0	193.69	0	31.97	4.97	4407.01
101	organic	7.58	44.30	114.50	0	0	37.99	2491.66	0	94.00	0	0	45.12	11.28
102	organic	28.06	211.83	447.63	0	61.48	100.65	1298.51	28.33	642.27	0	165.14	6617.87	3310.08
103	organic	12.56	188.04	236.70	950.59	69.77	127.06	800.53	8.15	170.98	0	124.66	17575.92	4749.28
104	organic	14.48	136.13	318.05	0	55.74	84.26	360.69	0	280.38	0	190.23	6397.70	11843.13
105	organic	12.46	151.53	248.88	0	2590	72.56	0	0	332.41	0	145.07	1681.25	5161.29
106	organic	10.62	116.40	167.66	0	0	57.49	0	5.25	90.57	0	46.81	1461.98	3876.18
101	AmFeOx	0	0.26	0.69		34.78	8.38	970.11	0	0.90	14.47	0	27.97	0
102	AmFeOx	9.28	0	129.06	1752.22	43.51	8.19	674.18	0	2.30	0	64.89	766.73	226.01
103	AmFeOx	0	0	60.35	0	47.27	6.87	529.65	0	0.81	0	0	3831.43	769.41
104	AmFeOx	0	0	45.06	0	0	6.08	386.18	0	1.05	0	0	490.74	584.56
105	AmFeOx	0	0	49.01	0	29.47	7.07	342.52	0	0.75	0	0	122.45	444.86
106	AmFeOx	0	0	0	0	0	8.04	155.96	0	0	0	0	110.92	311.26

Comments:

- To facilitate spreadsheet calculations of Kd values, zeros were entered in “below-detection limit” values.
- For Acid, Organic, and Amorphous Fe-oxide values that were below detection limit, 0 µg/L were entered to permit spreadsheet calculations of Kd_{max} values.

Appendix C3. Elemental Concentrations of Whole, <2-um, and 0.5-um Fractions of Sediment and Solid and Liquid Amounts Used in Total Dissolution Procedure

		Ag (ng/mL)	Cd (ng/mL)	Ce (ng/mL)	Hg (ng/mL)	Pb (ng/mL)	Sr (ng/mL)	Tl (ng/mL)	Th 232 (ng/mL)	U-235 (ng/mL)	U-238 (ng/mL)	Solids (g)	Liquid (mL)
101	Whole	0.009	0.003	2377	0.019	502	210	14.4	332	0.003	70	3.0634	25.00
	<2-um	209	0.003	5107	10	1241	412	62.6	506	0.003	146	1.9991	25.00
	<0.5-um	42	0.003	516	6	220	31	15.6	286	0.003	23	0.2893	25.00
102	Whole	170	32	5046	335	1659	744	7.1	18938	113	17681	2.3554	25.00
	<2-um	0.009	0.003	2729	0.019	0.013	0.007	0.006	11223	46	7355	1.2499	25.00
	<0.5-um	54	0.003	807	13	399	67	49.6	4004	0.003	2467	0.4830	25.00
103	Whole	0.009	0.003	1278	0.019	0.013	0.007	8.9	5608	241	32317	2.8338	25.00
	<2-um	172	8	1434	341	1453	627	85.1	108606	181	31990	1.8690	25.00
	<0.5-um	41	3	669	124	761	25.005	60.3	52264	85	15499	1.1011	25.00
104	Whole	74	1	1054	585	1066	423	8.8	70815	184	33544	2.5478	25.00
	<2-um	111	0.003	1766	314	1600	239	65.4	72078	385	54314	2.1205	25.00
	<0.5-um	37	0.003	804	138	832	112	51.2	40405	174	25346	1.2585	25.00
105	Whole	27	5	1595	582	1438	166	0.0	41359	427	59300	2.6508	25.00
	<2-um	102	8	3219	34	2665	230	56.6	5708	136	23391	2.2362	25.00
	<0.5-um	35	0.003	1385	15	1396	97	44.1	2966	61	10961	0.9796	25.00
106	Whole	36	6	3479	29	2636	329	14.1	3089	168	30465	2.6472	25.00
	<2-um	0.009	0.003	2136	0.019	1865	0.007	0.006	14280	416	55999	2.1660	25.00
	<0.5-um	0.009	0.003	897	0.019	858	0.007	0.006	6354	189	25403	1.0029	25.00

Comments:

- Bold values for water extracts are detection limits.

Table C4. Elemental Composition of Totally Digested (Aqua Regia) Samples of Intact Sediments

Sediment	Ag	Al	As	Ba	Be	Ce	Cr	Cu	Fe
101	0.49	1915.24	1.52	21.97	0.47	4.85	2.82	2.19	2634.83
102	2.18	6251.78	35.28	78.72	0.80	62.82	44.60	28.39	7533.14
103	0.53	2828.15	4.36	16.37	0.20	25.48	30.65	5.14	1797.92
104	2.03	2338.11	2.47	17.33	0.23	37.35	66.26	12.56	5490.17
105	1.30	3371.36	2.28	15.82	0.15	38.66	78.16	13.69	3885.48
106	0.57	4847.01	0.42	28.62	0.52	10.67	25.91	9.77	3793.74

Sediment	Hg	Mn	Ni	Pb	Sr	Tl	Th-232	U-235	U-238
101	0.03	84.28	1.45	0.00	1.46	10.94	2.32	0.00	3.78
102	6.82	114.37	15.97	49.83	7.16	16.16	231.08	1.07	171.00
103	0.52	25.11	4.26	44.27	3.20	11.83	871.16	1.93	415.57
104	9.45	20.84	8.34	63.71	3.61	13.16	241.97	4.12	613.63
105	9.20	22.18	5.41	58.95	1.31	14.36	61.29	1.52	298.06
106	0.64	13.52	7.45	15.96	2.59	17.42	51.18	1.94	303.38

Table C5. Correlation Coefficients Between COC Kd Values and Soil Properties (Excluded "Greater Than Kd Values" From These Calculations.

	<2-mm	Sand	Silt	Clay	pH	Organic C	CEC	AEC	Fe-oxides
Sand	-0.67	1.00							
Silt	0.12	-0.70	1.00						
Clay	-0.23	-0.38	0.21	1.00					
pH	-0.53	0.19	0.24	0.15	1.00				
Organic C	0.54	-0.35	-0.11	0.06	-0.97^(a)	1.00			
CEC	0.46	-0.86	0.92	0.11	0.14	-0.02	1.00		
AEC	0.21	-0.07	0.46	-0.76	0.03	-0.13	0.47	1.00	
Fe-oxides	0.40	-0.94	0.87	0.45	-0.05	0.24	0.89	0.13	1.00
Al-Kd	0.22	0.44	-0.71	-0.53	-0.71	0.56	-0.62	0.01	-0.57
Ba-Kd	0.99	-0.64	0.13	-0.28	-0.50	0.50	0.48	0.28	0.37
Be-Kd	0.86	-1.00	0.89	0.91	0.86	0.94	0.95	-0.49	1.00
Ce-Kd	0.15	-0.04	-0.22	0.00	-0.61	0.56	-0.25	-0.03	-0.11
Cr-Kd	0.02	0.53	-0.67	-0.45	-0.59	0.43	-0.64	0.02	-0.65
Cu-Kd	0.57	-0.48	-0.13	-0.13	-0.89	0.83	0.08	0.07	0.20
Fe-Kd	0.21	0.45	-0.76	-0.47	-0.68	0.54	-0.67	-0.09	-0.60
Mn-Kd	0.94	-0.75	0.11	0.08	-0.44	0.51	0.45	-0.09	0.49
Se-Kd	0.04	-0.66	0.65	0.67	0.55	-0.36	0.67	-0.21	0.71
Sr-Kd	0.95	-0.79	0.18	0.06	-0.43	0.50	0.52	-0.01	0.53
Th-Kd	0.52	0.08	-0.82	0.51	-1.00	0.98	-0.90	-0.57	-0.93
U238-Kd	-0.24	0.28	-0.12	0.08	-0.30	0.27	-0.37	-0.03	-0.24

	Al-Kd	Ba-Kd	Be-Kd	Ce-Kd	Cr-Kd	Cu-Kd	Fe-Kd	Mn-Kd	Se-Kd	Sr-Kd	Th-Kd	U-238
Ba-Kd	0.19	1.00										
Be-Kd	-0.98	1.00	1.00									
Ce-Kd	0.36	0.22	-1.00	1.00								
Cr-Kd	0.71	0.07	-0.76	0.94	1.00							
Cu-Kd	0.74	0.61	-1.00	0.88	0.83	1.00						
Fe-Kd	0.99	0.17	-0.96	0.30	0.69	0.67	1.00					
Mn-Kd	0.10	0.90	0.72	0.02	-0.17	0.45	0.12	1.00				
Se-Kd	-0.90	0.03	0.97	-0.74	-0.85	-0.80	-0.87	0.26	1.00			
Sr-Kd	0.02	0.94	0.92	0.17	-0.12	0.58	0.03	0.98	0.28	1.00		
Th-Kd	0.94	0.93	-1.00	0.87	0.85	0.91	0.78	0.29	-0.45	0.56	1.00	
U238-Kd	-0.03	-0.16	-1.00	0.92	0.83	0.64	-0.09	-0.37	-0.58	-0.23	0.78	1.00

^(a) In Bold Font: Correlation coefficients greater than 0.95, 0.88, 0.81 and 0.75, with 2, 3, 4, and 5 degrees of freedoms, respectively, are significant at P < 0.05 level (5% probability level).