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INFLUENCE OF DISSOLVED ORGANIC CARBON AND pH ON CONTAMINANT SORPTION TO SEDIMENT

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ACRONYMS

CDP	Cellulose Degradation Products
DOC	Dissolved Organic Carbon
ICP-MS	Inductively Coupled Plasma – Mass Spectrometry
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectrometry
K_d	Distribution Coefficient
LLW	Low Level Waste
NOM	Natural Organic Matter
PA	Performance Assessment
SRS	Savannah River Site
SR-NOM	Suwannee River Natural Organic Matter
XRD	X-ray Diffraction

1.0 ABSTRACT

Low-Level Waste buried on the SRS contains cellulosic materials, including wood, paper, and cardboard. Once buried, these materials are expected to degrade to form cellulose degradation products (CDP). Such materials are expected to influence radionuclide speciation in such a way that the radionuclides will sorb less to SRS subsurface sediments and therefore would migrate more rapidly from the disposal site. The objective of this study was to quantify through laboratory work the influence of CDP and pH on radionuclide sorption to SRS subsurface sediments.

The intent of this work was to create a K_d look-up table as a function of radionuclide, pH, and CDP concentration that could be used in future performance assessment calculations. Previous CDP-impacted K_d values were generated using two chemical analogues, UO_2^{2+} and Eu^{3+}. This study collected data from a wider range of analogues to validate and/or refine this approach. An incomplete-randomized-block-statistical design was used in a laboratory sorption study involving 2 soil types (sandy and clay textured), 5 dissolved organic carbon concentrations (a measure of CDP), and 3 pH levels. Non-radioactive solutes were used as chemical analogues to the radionuclides of interest to the Low-Level Waste Performance Assessment: monovalent cations (K^+ and Cs^+), divalent cations (Ni^{2+} and Sr^{2+}), trivalent cations (Ce^{3+} and Eu^{3+}), tetravalent cations (Th^{4+} and Zr^{4+}), and an anion (ReO_4^-). Analogues were matched to ~30 radionuclides based on similarities in periodicity and chemical properties. All CDP-impacted K_d values generated from this study were equal to or greater than those used in previous performance assessments. These larger K_d values may result in a greater Waste Acceptance Criteria (WAC), which in turn may permit greater amounts of Low-Level Waste to be safely disposed on site, saving the site the expense of shipping the waste off-site for disposal.

2.0 INTRODUCTION

2.1 CDP and Their Potential Impact on Radionuclide Sorption

Cellulosic materials (e.g., wood, paper, and cardboard products) readily degrade in the environment to form cellulose degradation products (CDP) in both the solid and dissolved (i.e., dissolved organic carbon; DOC) phases. Natural organic matter can greatly influence the speciation (i.e., chemical form) and mobility of nonradioactive elements (Perdue and Gjessing 1990, Thurman 1985, Stumm and Morgan 1981) and radioactive elements (Choppin 1988, Allard et al. 1989, Fairhurst et al. 1995; and Ledin et al. 1994). Co-disposal of radionuclides with cellulosic materials is, therefore, expected to influence nuclide fate and transport in the subsurface. The disposal and degradation of wood products in the E-Area slit trenches at the SRS are a source of organic matter that is expected to influence radionuclide fate and transport.

Insight into the fate of cellulosic material in SRS burial trenches can be drawn from the extensively studied behavior of natural organic matter in forested ecosystems. In both of these environments cellulosic materials are expected to decay to form a complex mixture of natural organic acids (e.g., humic and fulvic acids). These organic acids make up the majority of naturally occurring dissolved organic matter (Thurman, 1985). Even though organic matter will ultimately degrade to CO_2 or methane, steady state DOC concentrations in soil porewater exists as a result of plant (and to a smaller extent animal) detritus decomposition. DOC concentrations in wetlands are typically between 17 and 33 mg /L C (Thurman 1985). Subsurface groundwater typically contains about 0.7 mg/L C (Thurman 1985; Figure 1.1).

Major processes influencing the impact of natural organic matter on radionuclide/metal geochemistry are: 1) natural organic matter partitions to the sediment, thereby increasing the sorption capacity of the sediment, (2) natural organic matter decreases the system pH, generally decreasing cation sorption and increasing anion sorption, and (3) DOC complexes the radionuclide, thereby changing (generally decreasing) the tendency of the radionuclide to sorb to the sediment. These competing reactions can result in complex radionuclide sorption behavior. For example, Serkiz et al. (1998) reported that under low pH conditions, UO_2^{2+} sorption to kaolinite in the presence of DOC increased when compared to when no DOC was present. They attributed this to the DOC sorbing to the kaolinite and increasing the solid phase sorption capacity. At higher pH levels, where little C sorbed to the sediment, less UO_2^{2+} sorbed to the sediment in the presence of DOC than in its absence. They attributed this sorption behavior to the weaker tendency of DOC to sorb to kaolinite under higher pH conditions. The weaker tendency for DOC sorption resulted in greater DOC in solution to complex the UO_2^{2+}, thereby reducing the tendency for it to sorb.

Serkiz (2000) generated recommended K_d values for use in the Low-Level Waste Performance Assessment (PA) for a wide range of elements based on Cs, Eu, and U laboratory sorption test results. These provisional values were conservative because of the underlying assumptions. Briefly, the K_d values were assigned to a look-up table as a function of DOC or pH levels. K_d values of multivalent radionuclides were based on trends observed from CDP laboratory sorption experiments with U and Eu. He assumed that monovalent cationic radionuclides were influenced indirectly by CDPs' influence on pH, not by direct organic matter - cation interactions, i.e., the greater the CDP concentration, the lower the pH of the system. This assumption is based on the well established observation that monovalent cations form weak complexes to DOC. Specifically, monovalent cation K_d values were assigned based on trends observed with Cs^+ sorption to SRS sediments as a function of pH (Johnson 1995). This indirect approach was adopted in the absence of more direct data.

2.2 Previous Research Related to the Impact of CDP on Radionuclide Sorption to SRS Sediments

Serkiz and Myers (1996) modeled radionuclide sorption in the presence of CDP using available literature and limited site-specific data. This initial modeling used published stability constants for reactions between low molecular weight acids (i.e., citric acid and EDTA) and radionuclides to approximate behavior of CDP. Notable differences in the allowable radionuclide inventory of the E-Area slit trench were determined when the presence of cellulose degradation products (CDP) was accounted for in this conceptual model.

A series of laboratory studies were initiated in April 1998 to validate and/or update the modeling assumptions and results utilizing uranium (VI) and europium (III) as representative of divalent and trivalent radionuclides in the disposal environment (Serkiz et al. 1998). Phase I of this work employed a surrogate organic matter collected from the Suwannee River (SR-NOM) to represent the influence of CDP on nuclide sorption. This natural organic matter has been extensively characterized and is believed to resemble more closely the products from the degradation of cellulosic material than any single organic compound. These modeling studies clearly demonstrated that both pH and organic matter have a significant influence on Eu^{3+} and UO_2^{2+} mobility in SRS shallow waste burial environments.

Phase II of this work, investigated the major processes that influence nuclide transport in the presence of CDP (Serkiz et al. 1999). This work investigated: 1) the differences between laboratory-generated CDP and SR-NOM (used as a surrogate for CDP), especially as it related to Eu and U sorption 2) CDP sorption to SRS sediments, and, 3) radionuclide partitioning to sediments in the presence of CDP under a range of pH conditions. This work demonstrated that natural organic matter (SR-NOM) from the Suwannee River is an adequate surrogate for the radionuclide complexation chemistry of the mixture of organic compounds that comprise CDP under the conditions expected in SRS trenches. Furthermore, the concentration of CDP released from simulated cellulosic waste (paper, cardboard and wood) varied with time, decreasing as a function of increased leaching time. The amount of CDP sorbed to the sediments varied as a function of initial OM concentration, but was relatively independent of pH. Conversely, pH greatly influenced Eu sorption to SRS sediments, irrespective of whether CDP was presence or absent.

In previous modeling for the performance assessment (McDowell et al. 2000), it was assumed that cellulose materials degrade to constantly produce dissolved organic carbon at 30 mg /L C. It is clear from this laboratory work that the production of CDP is a dynamic process, producing under the conditions of these experiments concentration >1,000 mg/L C. Previous modeling also assumed a single pH value for the natural background to estimate contaminant sorption.

3.0 OBJECTIVE

The objective of this study was to measure sorption of Ce, Cs, Eu, Ni, K Rh, Sr, Th, and Zr as a function of pH and DOC to E-Area sediments. The intent of this research was to create a geochemical model that can be used in performance assessment calculations. Because it would be prohibitively expensive to conduct these tests using all the radionuclides included in the performance assessment (>25 elements), non-radioactive elements that are easily detectable by inductively coupled plasma – mass spectrometry (ICP-MS) were selected as chemical analogues. The valances of the analogues used in this study are:

- two monovalent cations, Cs^+ and K^+;
- two divalent cations, Ni^{2+} (transition metal) and Sr (alkaline earth);
- two trivalent cations, Ce^{3+} and Eu^{3+};
- two tetravalent cations, Th^{4+} (actinide) and Zr^{4+} (transition metal); and
- one anion, RhO_4^- (an analogue specifically for TcO_4^-).

Assignment of analogues to the radionuclides of interest to the Low-Level Waste Performance Assessment was based on similarities in periodicity (its location in the periodic chart) and chemical properties of the radionuclides (Table 1).

Table 1. Analogues of radionuclides of interest to the Low-Level Waste Performance Assessment.

Radionuclide	Assumed Valance	Analogue
Ac	+3	Ce & Eu
Am	+3	Ce & Eu
C[a]	-2	None
Cf	+3	Ce & Eu
Cm	+3	Ce & Eu
Cs	+1	Cs
H[a]	+1	None
I	-1	Re
Nb	+3	Ce & Eu
Ni	+2	Ni
Np	+1	Cs
Pa	+4	Th
Pb	+2	Ni
Pd	+2	Ni
Po	+2	Ni
Pu	+4	Th
Ra	+2	Sr
Rb	+1	Cs
Se	-1	Re
Sn	+2	Ni
Sr	+2	Sr
Tc	-1	Re
Th	+4	Th
U	+2	Sr
Zr	+4	Zr

(a) No attempt was made to use analogues to simulate carbon or hydrogen (tritium) because their chemistries are quite complicated and difficult to assess through the use of analogues.

4.0 MATERIALS AND METHODS

Details of the materials and methods are presented in section 8.0: Appendix A. A brief description of the experiment's materials and methods are described here. The experiment design was an incomplete factorial including two replicates, two sediments (sandy sediment and a clayey sediment from the E-Area subsurface environment), four pH levels, four DOC levels (Suwannee River Natural Organic Matter (reverse osmosis isolate) (SR-NOM); International Humic Substances Society, St. Paul, MN), and nine elements (Ce, Cs, Eu, Ni, K, Rh, Sr, Th, and Zr atomic absorption standards; Fisher Scientific, Pittsburgh, PA). Batch contact experiments were conducted in 50-mL centrifuge tubes with 5-g sediment and 50-mL liquid.

Complexity was added step-by-step to the system under study. Between each step, appropriate measurements were made to characterize the system. Initially, NaOH and HCl were added to a sediment – 0.02 M NaCl system to create the desired pH range of ~3 to 9. After a one-week equilibration period, pH levels were measured. Then varying concentrations of DOC were added to the pH adjusted tubes; after a one-week equilibration period, pH levels were measured. Finally, a concentrated solution containing the tracers was added to the system; after a 2-week equilibration period, pH, DOC, and aqueous metal concentrations were measured.

A number of control samples were also included. For the pH adjusted sediment-0.02 M NaCl system, no-sediment controls were included to permit calculating the zero-point-of-salt-effect (a measure of the pH level where the soil surface has a net zero charge). For the Sediment/0.02 M NaCl/DOC system, no-sediment controls (samples that were identical to the treatment samples except they did not contain any sediment) were included for all four DOC levels at the two extreme pH levels. For the Sediment/0.02 M NaCl/DOC/metals system, no-sediment controls were included for all 4 DOC levels at the two extreme pH levels.

DOC was measured using a standard C analyzer and metals were analyzed using an inductively-coupled plasma – mass spectrometer (ICP-MS). The ICP-MS samples were preserved in 0.5% HNO_3. The pH and DOC samples were not preserved in 0.5% HNO_3.

5.0 RESULTS

5.1 Sediment Properties

Two sediments were used in this study: a red clayey sediment (Subsurface Red Clayey Burial Ground Sediment) and a sandy sediment (BG1 Sandy Sediment) collected from the E-Area subsurface. These two sediments represent end-members with respect to contaminant sorption properties expected in the E-Area subsurface. The clayey sediment, as the name implies, has a higher concentration of fine particles and greater surface area than the sandy sediment (Table 2). Both sediments had similar pH values and no detectable organic matter. They also had essentially identical points-of-zero-salt effect of pH 5.5 to 6.5 (Figure 1 and Figure 2). The points-of-zero-salt effect provides an estimate of where the sediment has a net charge of zero, that is, the number of positive and negative surface charges are equal. The clayey sediment had XRD-detectable amounts of hematite and goethite, indicating they were present at concentrations • 5%. The sandy sediment was yellow, indicative of the presence of goethite; no hematite was detected by XRD. The titration curves of the two sediments showed that the red clayey sediment had appreciably more buffering capacity than the sandy sediment (i.e., more acid or base must be added to the clayey sediment than to the sandy sediment to produce the same pH change; Figure 3). The implication of this observation is that the red clayey sediment is less likely to undergo pH changes in response to varying CDP concentrations leaching from the low-level waste.

Table 2. Sediment characterization.

Parameter	Red Clay Sediment	Sandy Sediment(a)	Comment
pH	4.6	4.2	1:1 Sediment:water;
Sand / Silt / Clay (wt-%)	58 / 30 / 12	96 / 0 / 4	Mini-pipette method
Organic Matter (wt-%)	<0.01	<0.02	Combustion
Surface Area (m^2/g)	15.31	1.32(b)	BET
Mineralogy(c)	Kao > goeth > hem (no qtz or 1.4 nm peak)	kao = HIV >> goeth = qtz	XRD, 25 and 550 °C
Total Fe (wt-%)	5.97	NA	Total digestion, ICP-AES
Point-of-Zero-Salt-Effect(d)	5.6 to 6.2	5.5 to 6.5	Figure 1 & Figure 2

(a)) Kaplan 2003.

(b) Surface area was not measured on this sample. Provided is the average surface area of two sediments with similar particle size distributions and were also from the E-Area subsurface.

(c) kao = kaolinite, goeth = goethite, hem = hematite, qtz = quartz, HIV = hydroxyl-interlayered vermiculite.

(d) PZSE, provides an estimate of the pH at which the sediment surface has no net charge.

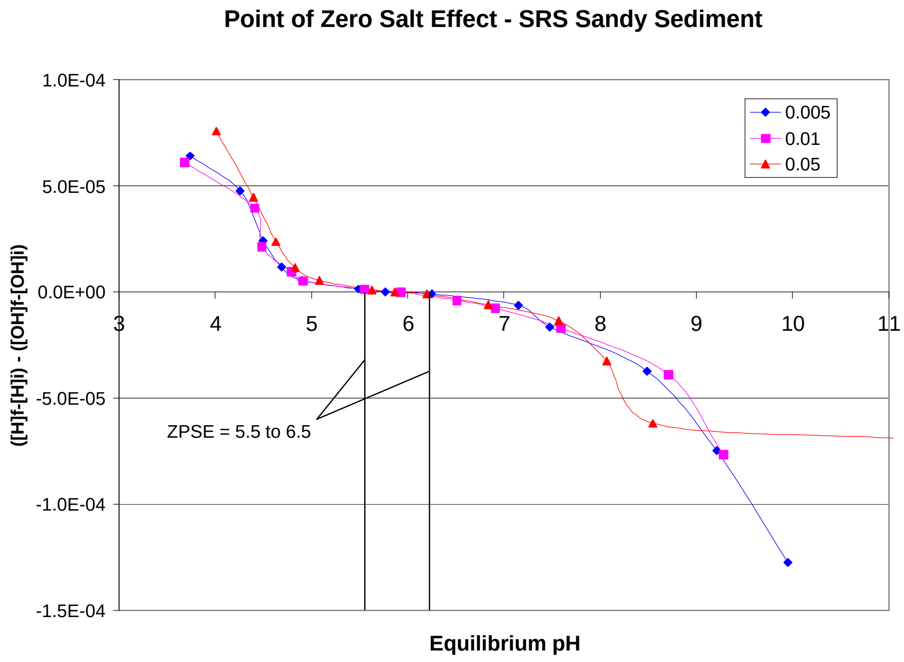


Figure 1. Point-of-Zero-Salt Effect (approximately the pH at which sediment has a net charge of zero) of the sandy sediment Conducted at 3 Ionic Strengths (the ZPSE is at pH 5.5 to 6.5).

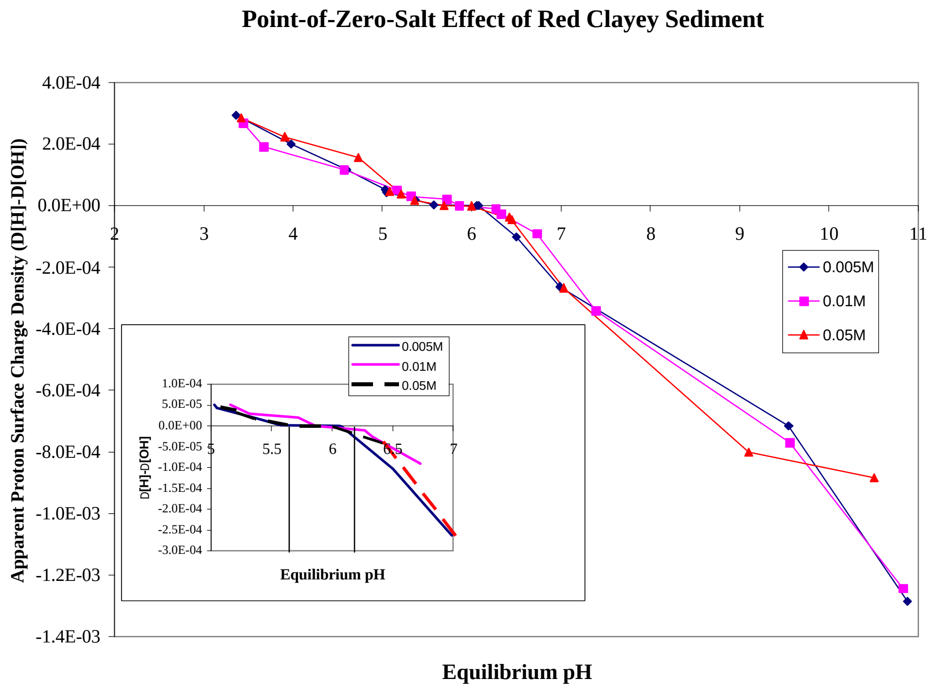


Figure 2. Point-of-Zero-Salt Effect for the Red Clay Sediment Conducted at 3 Ionic Strengths (PZSE = pH 5.6 to 6.2).

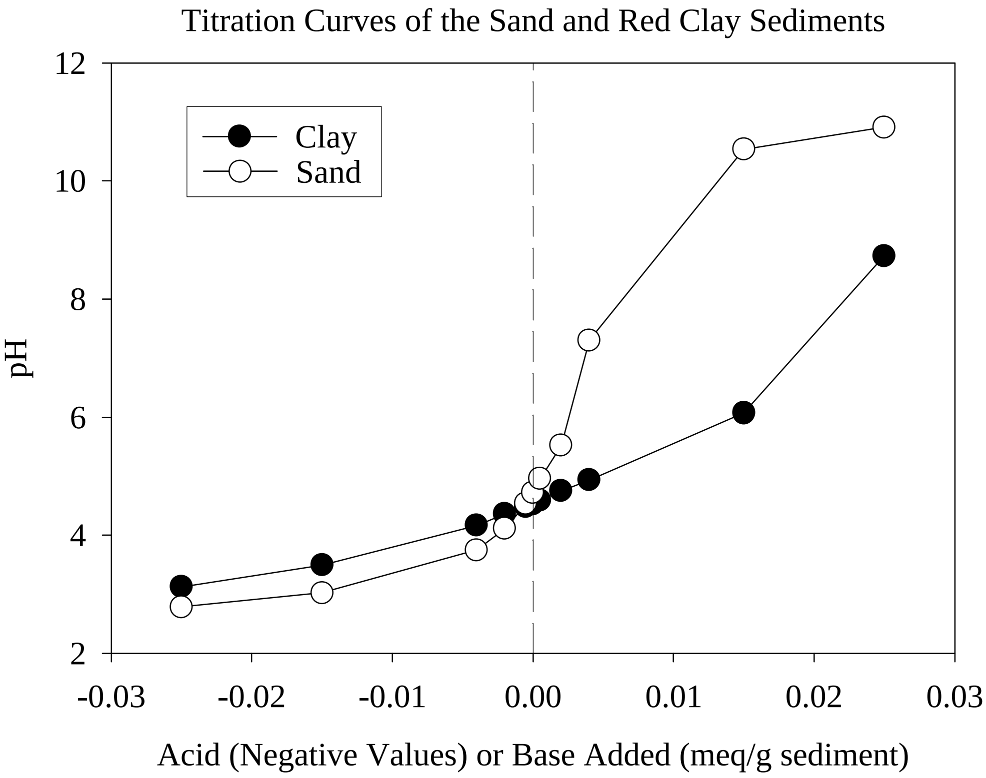


Figure 3. Titration of the sand and clay sediments.

5.2 Organic Matter Interactions with the Sediments

After the sediment suspensions were pH adjusted, varying amounts of SR-NOM were added to the tubes. The pH levels of the tubes were readjusted two more times within a one-week period. After this pH and SR-NOM equilibration period, the contaminants were introduced into the suspensions. The suspensions were pH adjusted for a forth time. The contaminants were then permitted to come to equilibration for another week. The DOC concentrations in the no-sediment controls are presented in Table 3. Except for the 0 mg/L C samples, the measured DOC concentrations were close to the targeted concentrations. This was unexpected considering that the amount of C in the SR-NOM had to be estimated and then there were a number of dilutions resulting from the various pH adjustments. The cause for the unexpected high DOC concentrations for the samples that did not receive any SR-NOM (0 mg/L C treatments) is not known, but needs to be further evaluated. There is no pH effect on DOC concentrations over the range of conditions in this experiment. This conclusion was anticipated but had to be confirmed prior to calculating the amount of organic carbon sorbed.

Table 3. Dissolved organic carbon concentrations in the no-sediment control samples (all treatments were duplicated).

pH	Targeted DOC Addition (mg/L C)	Measured DOC (mg/L C)
4.1	0	11 ± 1
	10	10 ± 1
	30	29 ± 4
	100	83 ± 4
	300	215 ± 16
7.4	0	5 ± 1
	10	11 ± 0
	30	28 ± 0
	100	107 ± 0
	300	230 ± 8
Average(a)	0	8 ± 1
	10	10 ± 1
	30	29 ± 2
	100	95 ± 2
	300	222 ± 12

(a) Averages are across both pH values (*n* = 4).

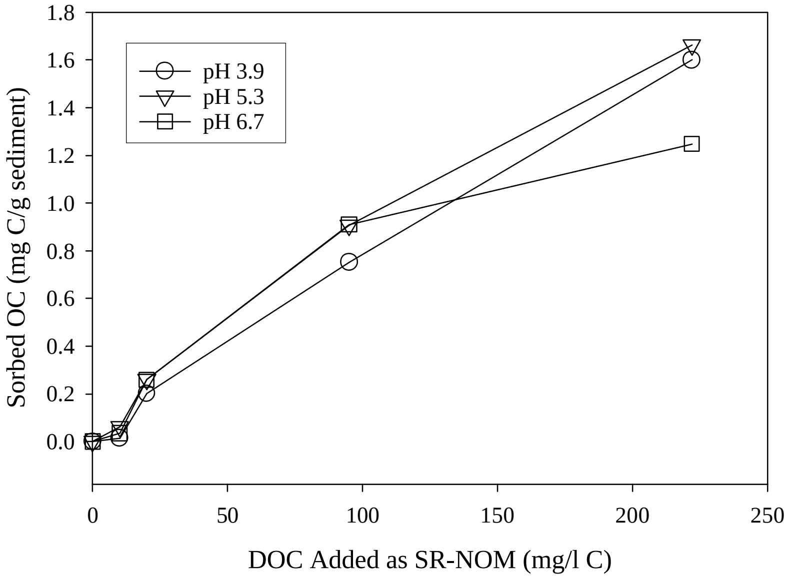
The average measured DOC values reported in Table 3 were used to calculate the amount of organic carbon, OC, sorbed on to the sediment by difference between the added DOC and the final solution DOC (Table 4 and Figure 4). Generally, there was more OC sorbed to the clayey than to the sandy sediment. Again, this was expected because of the greater surface area of the former sediment. There was also a tendency for more OC to be sorbed at lower pH levels, especially at lower DOC loadings. This trend may be attributed to anionic nature of various SR-NOM functional groups. This organic matter sorption data will be modeled in a subsequent study to be conducted in FY05.

Table 4. Dissolved and sorbed organic carbon concentrations at end of experiment.

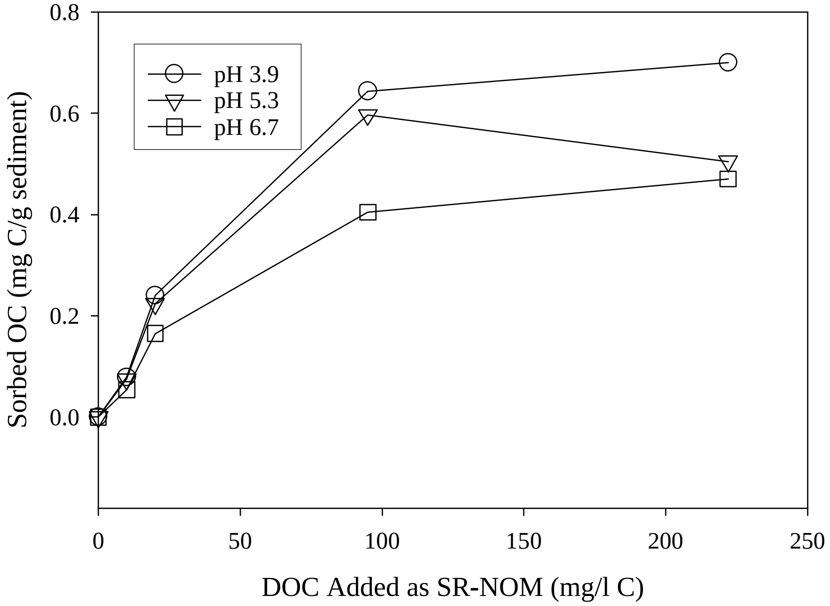
			Clayey Sediment		Sandy Sediment	
pH	Targeted DOC Addition (mg/L C)	Actual DOC Addition (mg/L C)	Final Measured DOC (mg/L C)	OC Sorbed (mg C/g sediment) [a]	Final Measured DOC (mg/L C)	OC Sorbed (mg C/g sediment) [a]
3.9	0	8	11 ± 0	0[b]	3 ± 1	0[b]
	10	10	9 ± 5	0.015	3 ± 0	0.079
	30	20	11 ± 2	0.201	7 ± 1	0.240
	100	95	28 ± 21	0.752	37 ± 3	0.644
	300	222	79 ± 4	1.600	160 ± 10	0.700
5.3	0	8	18 ± 2	0[b]	8 ± 0	0[b]
	10	10	5 ± 0	0.062	4 ± 0	0.075
	30	20	6 ± 0	0.260	9 ± 1	0.224
	100	95	14 ± 3	0.906	42 ± 8	0.597
	300	222	74 ± 4	1.662	177 ± 16	0.505
6.7	0	8	11 ± 1	0[b]	2 ± 1	0[b]
	10	10	7 ± 2	0.035	6 ± 1	0.054
	30	20	6 ± 1	0.259	14 ± 0	0.165
	100	95	14 ± 1	0.910	59 ± 4	0.405
	300	222	111 ± 20	1.248	180 ± 10	0.470

[a] OC Sorbed is based on “Actual DOC Addition.” It reflects an average value based on an average aqueous volume of 55.9 mL/tube and suspension load of 5.000 g/tube.

[b] Due to analytical uncertainty associated with the Actual DOC Addition when no DOC was added, OC Sorbed was assumed equal to zero mg C/g sediment.



Sorbed OC vs. Added DOC: Clayey Sediment



Sorbed OC vs. Added DOC: Sandy Sediment

Figure 4. Sorbed organic carbon vs. dissolved organic carbon added in the clayey sediment (top) and sandy sediment (bottom).

5.3 Contaminant Sorption in the Presence of Varying pH and DOC Concentrations

5.3.1 pH and SR-NOM Controls

A number of controls were included in this study, approximately 1 control for every 3 samples. One set of controls ran along side the samples were the no-sediment controls. These controls were treated identically as the other samples except that they did not include any sediment. They were adjusted to two pH values, pH 4.1 and 7.4. By not including the sediment, it is possible to separate chemical reactions involving sediments from those that do not involve sediments.

The pH values were adjusted by adding either NaOH or HCl to solutions containing varying concentrations of SR-NOM. The pH was adjusted and permitted to come to a steady state for one week prior to introducing the contaminants. Upon adding the contaminants, the pH was again adjusted. The final pH values of these controls as a function of SR-NOM concentrations are reported in Figure 5. This shows that the pH values remained essentially constant as a function of targeted SR-NOM concentration. The importance of this is that the natural tendencies of pH values decreasing as SR-NOM concentrations increase were overcome by acid and base additions. Thus, SR-NOM and pH were in fact independent variables in this set of controls, consistent with the experimental design.

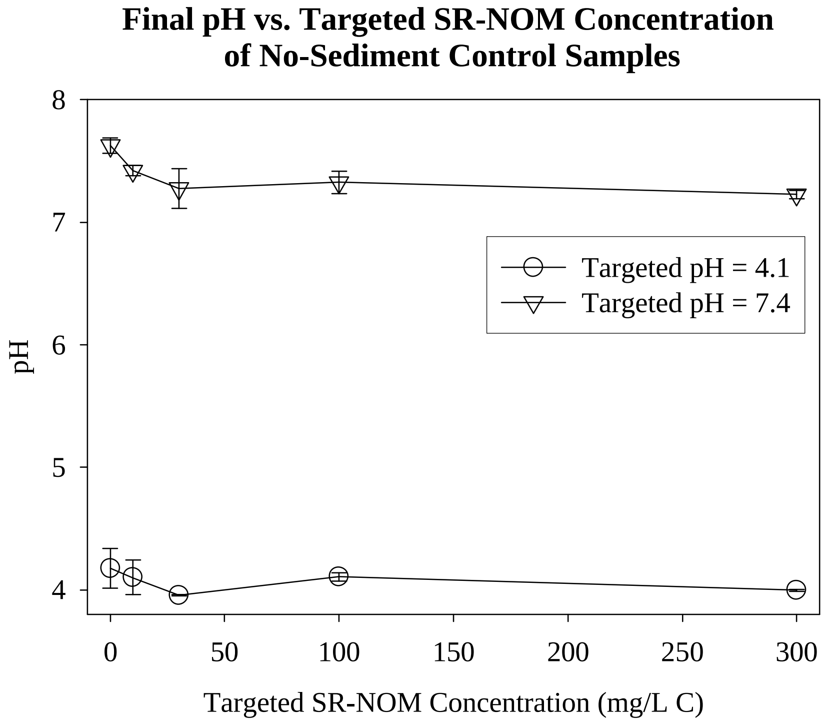


Figure 5. Final pH vs. targeted SR-NOM concentration of no-sediment control samples (2 observations for each mean and standard deviation).

5.3.2 Contaminant Spike Controls

Another concern regarding the contaminant spikes, was to determine how soluble they remained as a function of pH and SR-NOM. Conclusions regarding these controls are listed below.

- The ICP-MS did not detect any rhenium in the controls (or sediment samples) (data presented in section 9.0, Appendix B). Rhenium was somehow lost from the sample during the experiment or, more likely, an analytical issue existed whereby Re could not be detected. Rhenium data will therefore not be discussed further.
- The K control data indicated that some K was introduced into the system though sources other than the spike (data presented in section 9.0, Appendix B). The sediment and SR-NOM contained K, and it was anticipated that they may desorb some K into the aqueous phase. Unfortunately, this occurred in an apparently non-systematic manner, thus precluding further evaluation of these data.
- Cs, Ni, and Sr aqueous concentrations at pH 4.1 remained fairly constant as a function of SR-NOM concentrations. Considering the means and standard deviation bars, there was not a systematic change in solute concentrations as a function of SR-NOM concentrations (Figure 6).
- Cs, Ni, and Sr aqueous concentrations at pH 7.4 also did not show any systematic change with SR-NOM concentrations (Figure 7). However, the standard errors were quite large in one case (Ni in the 100 mg/L C treatment). There may have been some Ni that precipitated from solution in the 0 mg/L C treatment, but not in any of the other SR-NOM treatments.
- Ce, Eu, Th, and Zr aqueous concentrations at pH 4.1 remained constant as a function of SR-NOM concentration (Figure 8). Contaminant concentration variability in these samples was quite low.
- Ce, Eu, Th, and Zr aqueous concentrations at pH 7.4, varied greatly as a function of SR-NOM concentrations (Figure 9). At 0 mg/L C treatments, aqueous concentrations were significantly lower that the other SR-NOM treatments. This may be the result of the contaminants precipitating out these elements. When SR-NOM concentrations were sufficiently high, these elements were presumably solubilized by solution complexation with the SR-NOM. Presumably, the SR-NOM complexation reaction was able to out-compete the hydrolysis precipitation reaction, thereby permitting the contaminant to remain in solution as a SR-NOM complex.

To evaluate which phases may have precipitated out of solution in the pH 7.4, no SR-NOM solutions, thermodynamic calculations were conducted using the software Visual MINTEQA2 (Gustaffsson 2003) to calculate the saturation index (Eq. 1):

$$Saturation\ Index = \log\left(\frac{IAP}{K_s}\right) \tag{1}$$

where IAP is the ion activity product (the product of the reactants raised to their stoichiometric power) and K_s is the solubility constant of the solid. When the saturation index = 0, the system is at equilibrium with respect to that solid. When the saturation index is >0, the solid phase is supersaturated with respect to that solid and is inclined to precipitate. When the saturation index is <0, the solid phase is undersaturated with respect to the solid. All solids with a saturation index near or greater than 0 are presented in Table 5. Given the uncertainty of the analytical results and the thermodynamic constants that go into making this calculation, any of these solids may have precipitated from solution. Conclusions regarding these thermodynamic calculations for the experimental conditions employed in this study are listed below.

- Cs, Sr, or Ni solid phases were not expected to form.
- Trivalent (Ce^{3+} and Eu^{3+}) and tetravalent (Th^{4+} and Zr^{4+}) cations were the most likely to precipitate at pH 7.4,
- With the exception of ThO_2, no solids were supersaturated at pH 4.1.

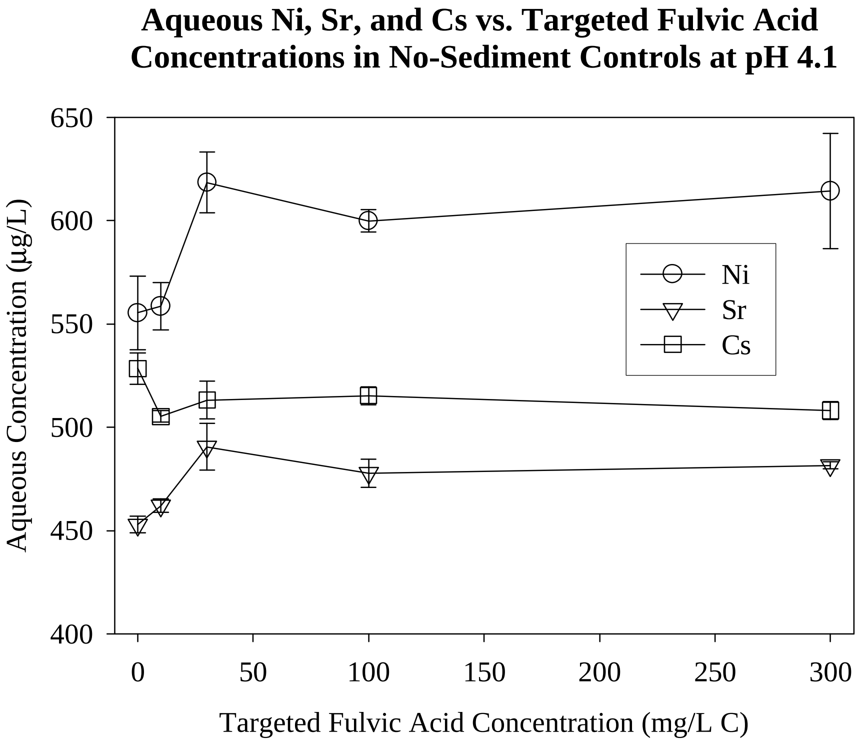


Figure 6. Aqueous Ni, Sr, and Cs versus targeted SR-NOM concentrations in the no-sediment controls at pH 4.1.

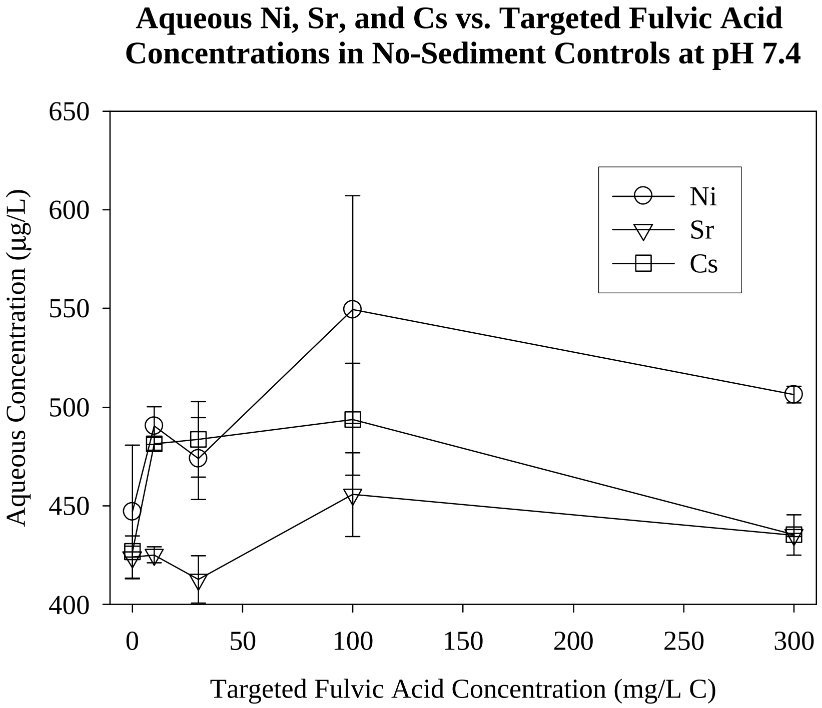


Figure 7. Aqueous Ni, Sr, and Cs versus targeted SR-NOM concentrations in no-sediment controls at pH 7.4.

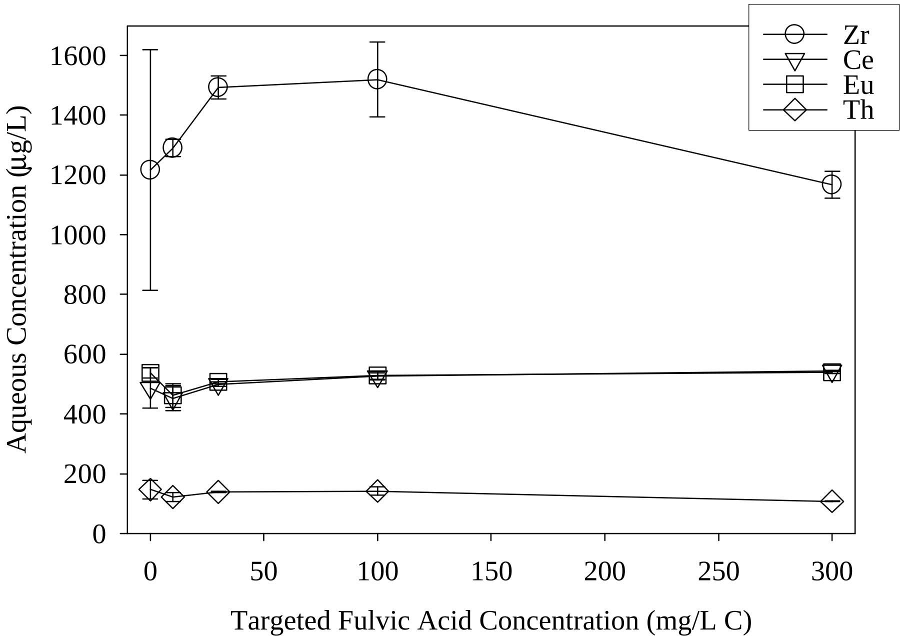

Aqueous Ce, Eu, Th, and Zr vs. Targeted Fulvic Acid Concentrations in No-Sediment Controls at pH 4.1

Figure 8. Aqueous Ce, Eu, Th, and Zr versus targeted SR-NOM concentrations in no-sediment controls at pH 4.1.

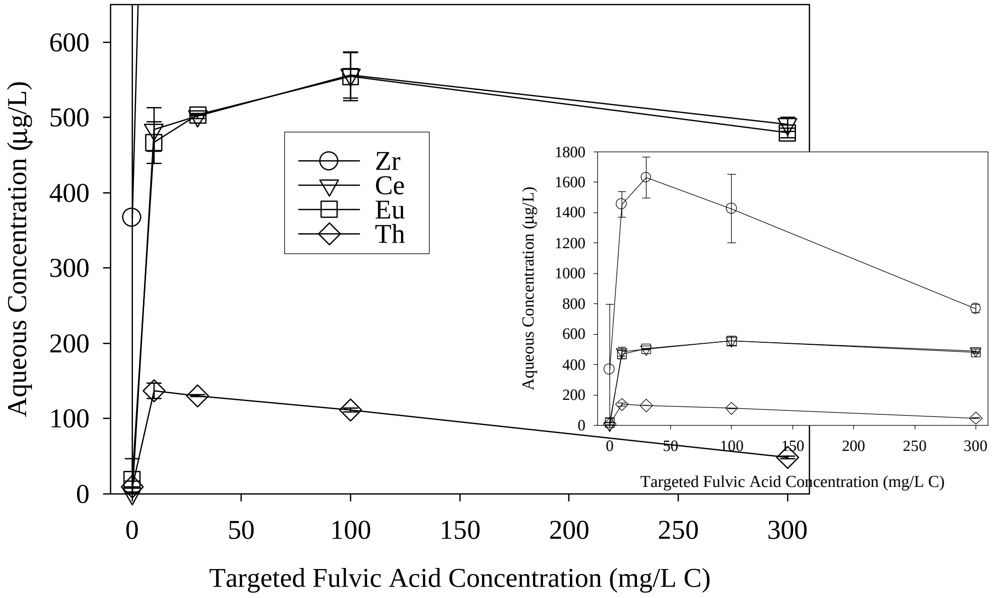

Aqueous Ce, Eu, Th, and Zr vs. Targeted Fulvic Acid Concentrations in No-Sediment Controls at pH 7.4

Figure 9. Aqueous Ce, Eu, Th, and Zr versus targeted SR-NOM concentrations in the no-sediment controls at pH 7.4.

Table 5. Thermodynamic calculations of the saturation index of the no-sediment control solutions.

pH	Solid phase	log (Ion Activity Product)	Saturation Index: $\log(IAP/K_s)^{(a)}$
4.1	ThO_2	8.3	2.0
7.4	$Eu(OH)_3$	16.1	-0.3
	$Ce(OH)_3$	16.7	1.0
	$Th(OH)_4$	15.2	3.9
	ThO_2	15.2	8.9
	ZrO_2	1.7	-0.2

(a) When the saturation index = 0, the system is at equilibrium with respect to that solid. When the saturation index is >0, the solid phase is supersaturated and is inclined to precipitate. When the saturation index is <0, the solid phase is undersaturated.

5.3.3 Monovalent Cation Sorption

Monovalent cation radionuclides of interest to the LLW-PA are Cs^+, NpO_2^+, and Rb^+ (**Table 1**). There were two monovalent cations included in this study as analogues for these radionuclides, Cs^+ and K^+. Unfortunately, the K^+ data are unreliable because K^+ was introduced into the system during the course of the study, likely from the sediment, SR-NOM, and to a lesser extent, as impurities in chemicals. This does not compromise the results greatly because stable Cs is a perfect analogue for radioactive Cs, and a close chemical analogue for Rb, which exists just above it on the periodic chart. Cesium is not an especially good analogue for NpO_2^+ due to the disparity between their sizes, ionization energies, and nuclear charges.

Cesium K_d values changed in a rather systematic way with pH, sediment type, and SR-NOM concentrations (Figure 10):

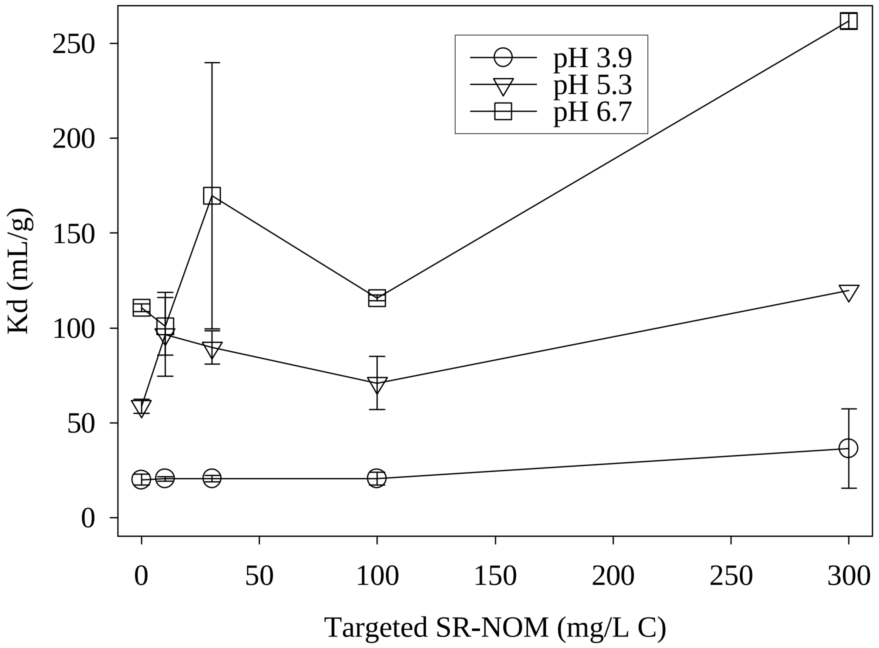
- Cs K_d values were 2 to 3 times greater in the clayey than in the sandy sediment,
- Cs K_d values increased with pH, and
- Cs K_d values increased with SR-NOM concentrations.

Of these findings, the latter one is of greatest importance because the performance assessment presently assumes the opposite trend, namely that Cs K_d decreases as SR-NOM concentrations increase. The cause for this disparity is not known but may be attributed to the fact that Cs has a weak tendency to complex with SR-NOM, and as such, as the SR-NOM concentrations in solution increase we do not observe a concomitant increase in solution Cs concentrations. The weak tendency for Cs to form complexes to humic materials is shown by the following ranking of cations by their propensity to form complexes with humic materials (Bovard et al. 1970):

$$Cd^{3+} > Fe^{3+} > Co^{2+} \bullet Ru^{2+} \bullet Sr^{2+} > Cs^{+}. \qquad (2)$$

Furthermore, complexation of Cs by common industrial chelates (e.g., EDTA) is believed to be poor due to their low stabilities and the presence of competing cations (e.g., Ca^{2+}) at appreciably higher concentrations than that of Cs. The data may suggest that Cs bonds stronger to SR-NOM coated soils than the original soil surface itself. Stated differently, Cs may complex better with sorbed SR-NOM than to dissolved SR-NOM.

Cs Sorption to the Clayey Sediment
as a Function of pH and SR-NOM Concentrations



Cs Sorption to the Sandy Sediment
as a Function of pH and SR-NOM Concentrations

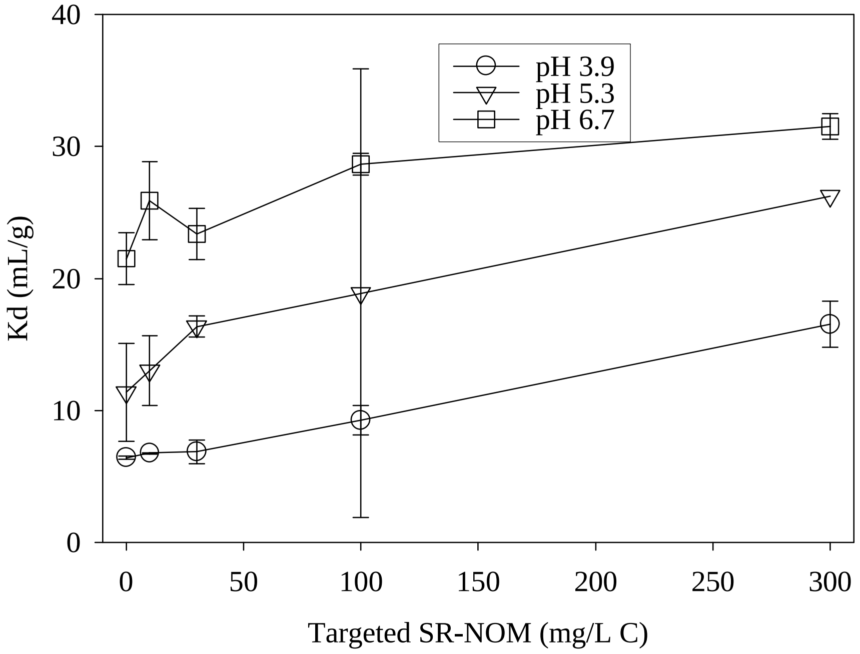


Figure 10. Cs K_d values as a function of pH and SR-NOM concentrations in clayey (top) and sandy (bottom) sediments.

5.3.4 Divalent Cation Sorption

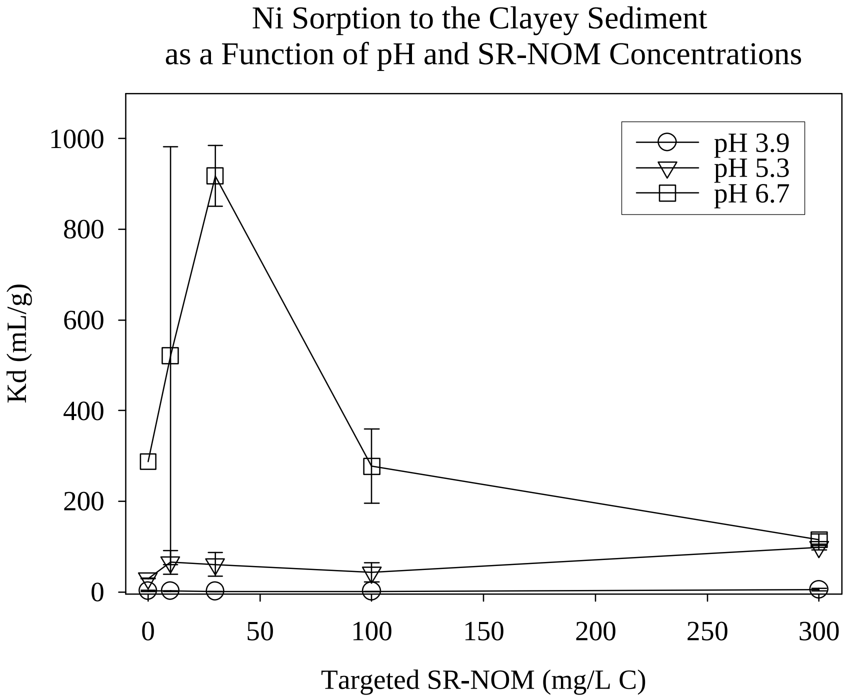
Divalent cation radionuclides of interest to the LLW-PA are Ni^{2+}, Pb^{2+}, Pd^{2+}, Po^{2+}, Ra^{2+}, Sn^{2+}, Sr^{2+}, and UO_2^{2+} (**Table 1**). There were two divalent cations included in this study as analogues for these radionuclides, Ni^{2+} and Sr^{2+}. Stable Ni^{2+} was used directly to provide K_d values for radioactive Ni, and as an analogue for Pb, Pd, Po and Sn. Similarly, stable Sr^{2+} will be used directly to provide K_d values for radioactive Sr, and as an analogue for Ra^{2+} and UO_2^{2+}. Previously, data on the influence of CDP on UO_2^{2+} sorption to kaolinite were reported in Serkiz (2000). The assignment of the analogues to the radionuclides was based upon periodicity (its location in the periodic chart) and chemical properties of the radionuclides, as compared to those of the analogue.

Nickel K_d values (Figure 11, Table 6) followed similar trends with pH and sediment type as described for Cs (Figure 10; Section 5.3.3):

- Ni K_d values increased with pH,
- Ni K_d values were 2 to 3 times greater in the clayey than in the sandy sediment (except at pH 3.9).

Nickel K_d values had a more complicated trend with SR-NOM concentrations than was observed with Cs K_d values. First, there was an interactive effect between pH and SR-NOM on Ni K_d values. As the pH increased, there was a greater impact of SR-NOM concentrations on Ni K_d values. At pH 3.9, there was essentially no Ni sorption occurring in either sediment and there was no significant ($P \leq 0.05$, df = 4) correlation between Ni K_d values and targeted SR-NOM concentrations. The average Ni K_d value across all SR-NOM concentrations in the sandy sediment was 2.5 ± 2.0 mL/g and in the clayey sediment was 2.4 ± 1.6 mL/g (Table 6). At pH 5.3, there were measurable amounts of Ni sorbed to the sediments, but there was no significant ($P \leq 0.05$, df = 4) correlation between targeted SR-NOM concentrations and K_d values. At pH 5.3, the average Ni K_d value across all SR-NOM concentrations in the sandy sediment was 9.6 ± 2.4 mL/g and in the clayey sediment was 59.4 ± 26.1 mL/g (Table 6).

At pH 6.7, the Ni K_d values were generally greater than at the lower pH levels. In the sandy sediment, the overall Ni K_d was 128 ± 110 mL/g, whereas in the clayey sediment it was 423 ± 312 mL/g. The large standard deviation can be attributed to the large fluctuations with SR-NOM additions. The trend between Ni K_d values and SR-NOM concentrations (Figure 11) is one that was observed with several of the other analytes. When no SR-NOM was added, a relatively low K_d value was observed. Upon adding a little SR-NOM, between 10 or 30 mg/L C, an increase in sorption was observed. SR-NOM additions >~30 mg/L C, result in a steady decline in K_d values, to values lower than those for the 0 mg/L C treatment. One possible explanation for this trend is that at low SR-NOM additions, a greater fraction of the SR-NOM sorbs to the sediment thereby increasing the relative number of organic sorption sites on the solid phase over that in solution. SR-NOM sorption was shown in section 5.2 to be very pH dependent, consistent with the apparent trends in Figure 11. At higher organic matter loadings, the concentration of SR-NOM may have increased in the aqueous phase, promoting SR-NOM-Ni solution complexation. Consistent with this explanation is that the maximum K_d in the sandy sediment is at 10 mg/L C, whereas in the clayey sediment, which contains a greater number of Ni and SR-NOM sorption sites, the maximum K_d is much greater and occurs at 20 mg/L C (Figure 11). Importantly, not all SR-NOM additions decreased K_d values. Such decreases in K_d values were observed only at higher SR-NOM concentrations. Also, these decreases were observed only in the high pH system. The low pH systems showed no apparent correlation between K_d and SR-NOM concentrations.



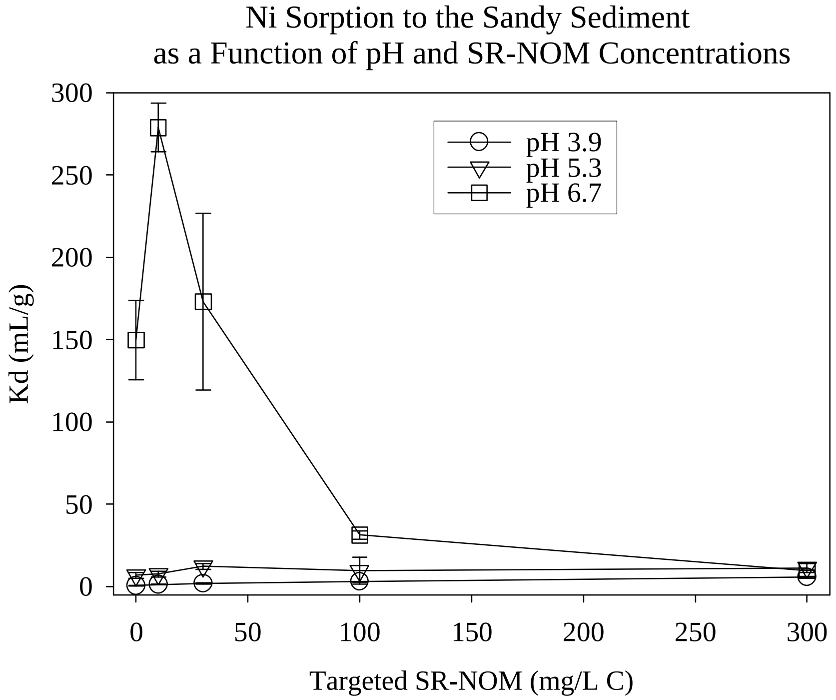


Figure 11. Ni K_d values as a function of pH and SR-NOM concentrations in clayey (top) and sandy (bottom) sediments.

Table 6. Ni K_d values (mL/g).

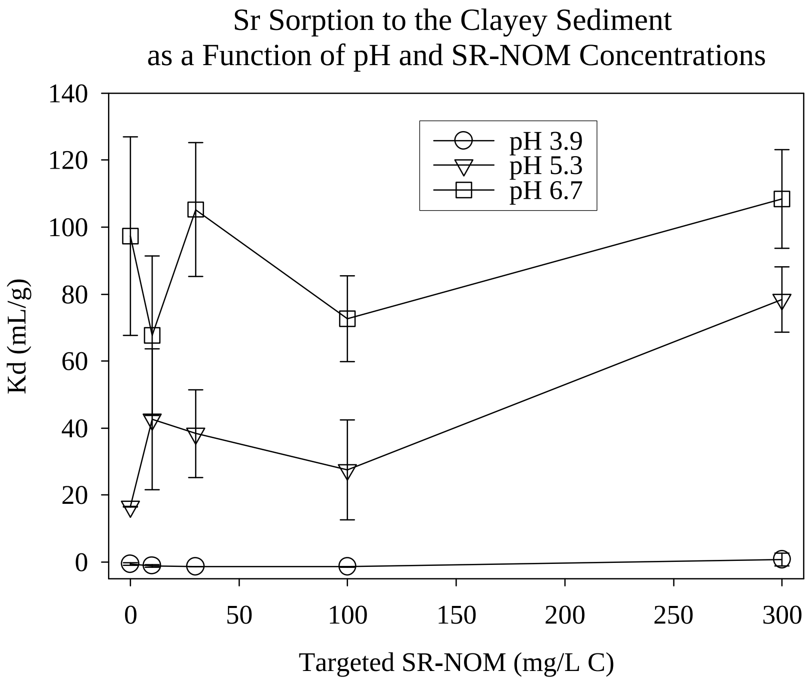
Target SR-NOM (mg/L C)	Clayey Sediment						Sandy Sediment					
	pH 3.9		pH 5.3		pH 6.7		pH 3.9		pH 5.3		pH 6.7	
	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.
0	2.3	0.8	29.5	0.8	287.3	0.0	0.6	0.3	6.8	1.6	149.8	24.2
10	1.8	0.5	65.3	25.9	521.0	460.3	1.3	0.3	7.7	1.8	278.8	14.8
30	1.1	0.0	60.8	25.9	917.7	66.5	1.8	0.4	12.4	1.7	173.1	53.6
100	1.6	0.0	43.0	21.0	277.0	81.9	2.9	0.1	9.6	8.1	31.4	2.5
300	5.1	2.9	98.7	5.9	115.3	12.2	5.8	0.3	11.4	2.8	9.8	0.2
Avg.	2.4		59.4		423.7		2.5		9.6		128.6	
Stdev.	1.6		26.2		311.8		2.0		2.4		110.2	

Strontium K_d values in the clayey sediment exhibited no discernable trends with respect to SR-NOM concentrations (Figure 12 and Table 7), i.e., there were no significant differences in the means of Sr K_d values based on Dunnett's test for comparing means to a control ($p \leq 0.05$, n = 8). However, two conclusions can be made from this data.

- As pH increased, Sr K_d values increased.
- The clayey sediment sorbed more Sr than the sandy sediment.

Sr K_d values in the sandy sediment (Figure 12 and Table 7) followed similar trends as those observed for Ni K_d values in the sandy sediment (Figure 11 and Table 6). These trends in the sandy sediment are listed below.

- Sr K_d values increased as pH of the system increased.
- There was an interactive effect of pH and SR-NOM concentration on Sr K_d values.
- At pH 3.9, little Sr was sorbed, irrespective of SR-NOM concentrations.
- At pH 5.3, Sr K_d values increased with SR-NOM concentrations.
- At pH 6.7, there was a maximum Sr K_d value obtained at 10 mg/L C SR-NOM, followed by a systematic decrease in Sr K_d values as the SR-NOM concentrations increased. The Sr K_d value for the highest SR-NOM concentration, 300 mg/L C, were less than that measured in the 0 mg/L C SR-NOM treatment.



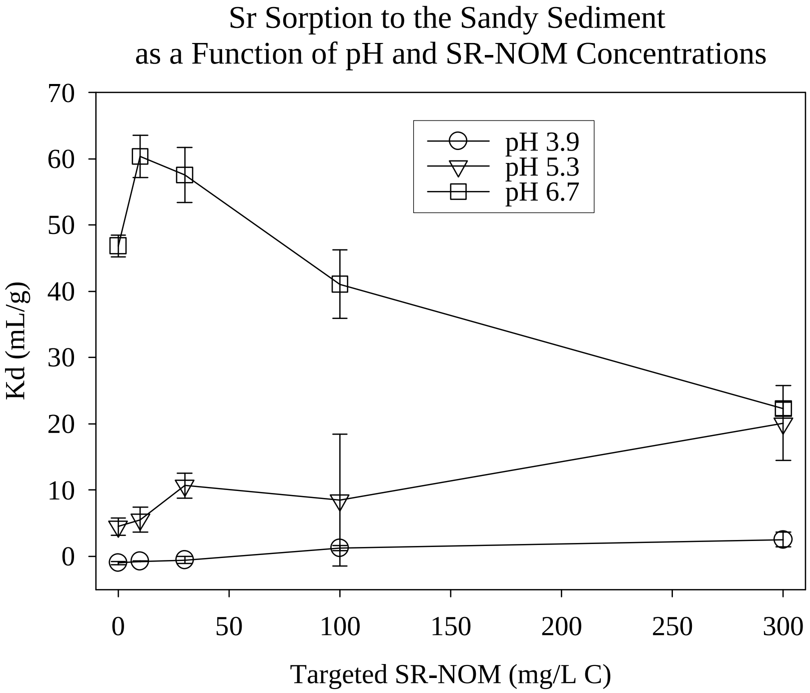


Figure 12. Sr K_d values as a function of pH and SR-NOM concentrations in clayey (top) and sandy (bottom) sediments.

Table 7. Sr K_d values (mL/g).

Target SR-NOM (mg/L C)	Clayey Sediment						Sandy Sediment					
	pH 3.9		pH 5.3		pH 6.7		pH 3.9		pH 5.3		pH 6.7	
	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.
0	-0.6(a)	0.4	16.6	0.0	97.4	29.6	-1.0	0.3	4.5	1.3	46.9	1.7
10	-1.1	0.4	42.6	21.1	67.7	23.8	-0.8	0.0	5.5	1.9	60.4	3.2
30	-1.3	0.0	38.3	13.1	105.3	20.0	-0.6	0.5	10.7	1.9	57.6	4.2
100	-1.4	0.1	27.5	14.9	72.7	12.8	1.2	0.4	8.5	10.0	41.1	5.2
300	0.7	1.9	78.4	9.7	108.4	14.8	2.5	1.1	20.1	5.7	22.3	1.0
Avg	-0.7		40.7		90.3		0.3		9.8		45.6	
Stdev	0.9		23.4		18.9		1.5		6.2		15.2	

(a) Negative K_d values can be attributed to analytical error.

5.3.5 Trivalent Cation Sorption

Trivalent cation radionuclides of interest to the LLW-PA are Ac^{3+}, Am^{3+}, Cf^{3+}, Cm^{3+}, and Nb^{3+} (Table 1). Two trivalent cations were included in this study as analogues for these radionuclides, Ce^{3+} and Eu^{3+}. Cerium and Eu are both lanthanides, and as such would be expected to interact with ligands and sediment in a similar manner to each other. So they do not represent a wide range of geochemical behaviors of trivalent cations.

Cerium (Figure 13 and Table 8) and europium (Figure 14 and Table 9) K_d values followed nearly identical trends with pH, sediment type, and SR-NOM concentrations. Furthermore these trends were similar to those of Ni (Figure 11) and Sr (Figure 12; sandy sediment only).

- Ce and Eu K_d values were higher in the clayey sediment than in the sandy sediment.
- Ce and Eu K_d values increased with increasing pH.
- There was a pH and SR-NOM concentration interactive effect on Ce and Eu K_d values. As pH increased, there was a greater SR-NOM effect on Ce and Eu K_d values, especially true in the sandy sediment. At pH 3.9, SR-NOM concentration did not have an effect on Ce K_d values.
- Ce and Eu K_d values had a strong dependence on SR-NOM concentrations. Small additions of SR-NOM to the system, 10 mg/L C, caused the K_d values to increase sharply compared to when no SR-NOM was in the system. Additions of greater concentrations of SR-NOM caused incrementally larger decreases in K_d values. At SR-NOM additions • 100 mg/L C, the K_d values decreased below those for when no SR-NOM was in the system. Very similar trends were reported for Eu K_d by Serkiz (2000).

Not surprisingly, Ce and Eu K_d values were very large. What was surprising was just how sensitive the values were to pH and SR-NOM concentrations. For example, at 0 mg/L SR-NOM, the Ce K_d values in the clayey sediment increased from 36 to 19,000 mL/g as the pH increased from 3.9 to 6.7. Similarly, at pH 6.7, Ce K_d values in the clayey sediment varied from 105 to >29963 mL/g with change in SR-NOM concentrations.

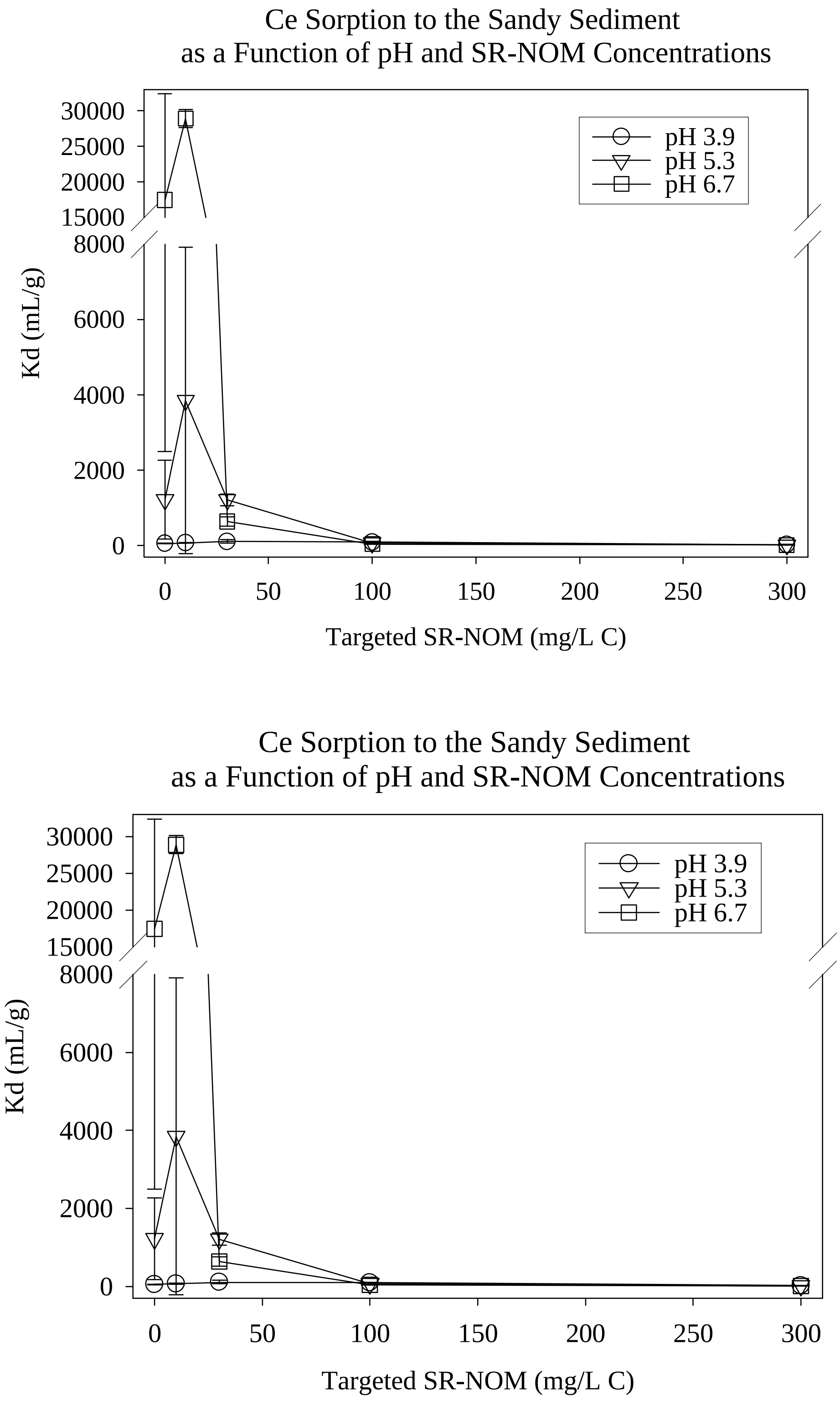
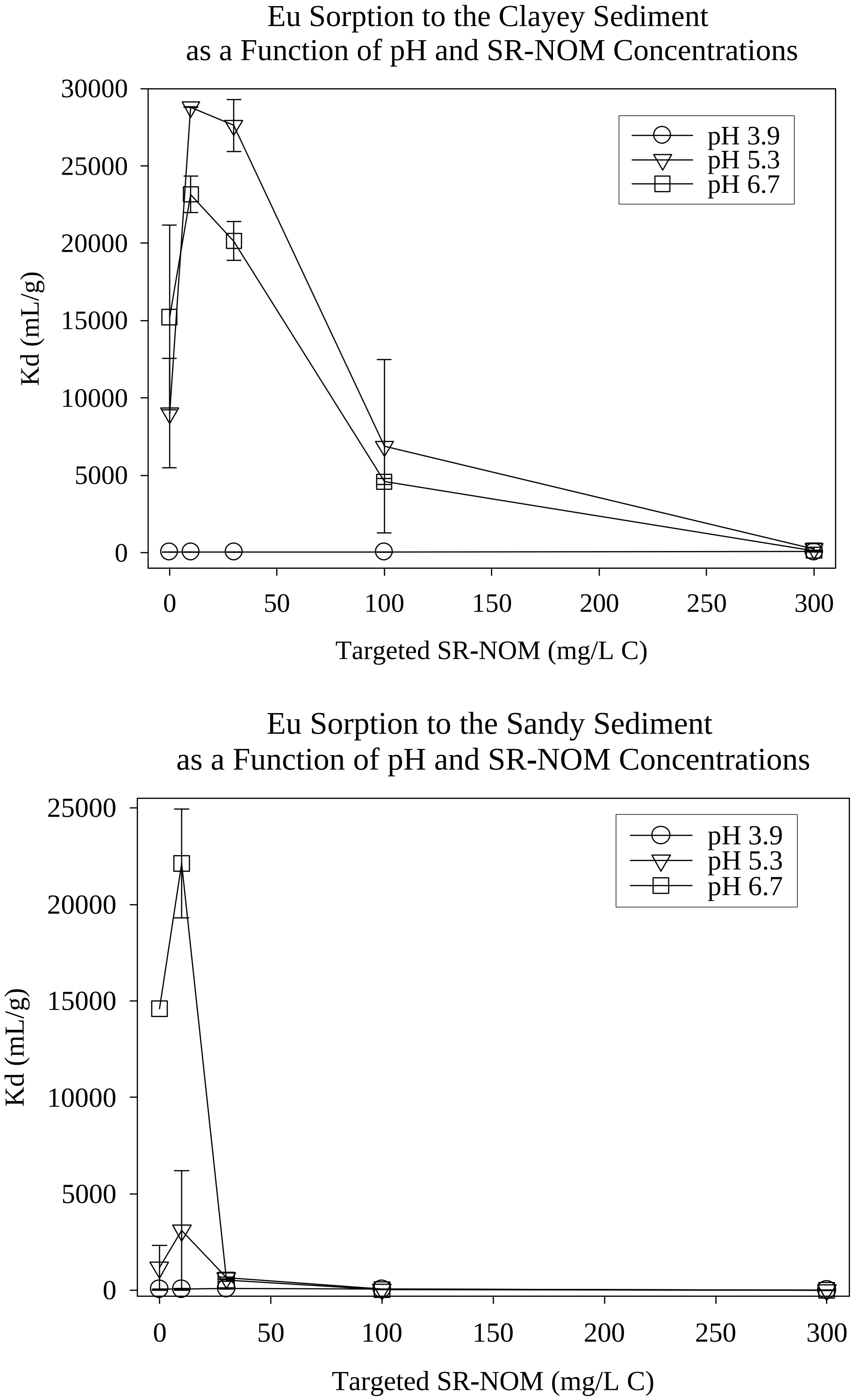


Figure 13. Ce K_d values as a function of pH and SR-NOM concentrations in clayey (top) and sandy (bottom) sediments (all K_d values >25,000 mL/g are greater-than values).

Table 8. Ce K_d values (mL/g).

Target SR-NOM (mg/L C)	Clayey Sediment						Sandy Sediment					
	pH 3.9		pH 5.3		pH 6.7		pH 3.9		pH 5.3		pH 6.7	
	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.
0	36	8	8687	4980	19343	9316	49	7	1220	1042	17450	14961
10	26	1	>28020	12	>29963	1934	68	12	3845	4067	>28918	1257
30	33	4	>22913	7242	>27481	1985	107	45	1210	157	638	122
100	40	4	4960	1690	7822	1694	92	9	69	22	37	3
300	71	27	361	180	105	14	21	4	14	3	10	0
Avg	41		12988		16943		67		1272		9411	
Stdev	18		11904		12777		34		1554		13213	


Eu Sorption to the Clayey Sediment as a Function of pH and SR-NOM Concentrations

Eu Sorption to the Sandy Sediment as a Function of pH and SR-NOM Concentrations

Figure 14. Eu K_d values as a function of pH and SR-NOM concentrations in clayey (top) and sandy (bottom) sediments (all K_d values >20,000 mL/g are greater-than values).

Table 9. Eu K_d values (mL/g).

Target SR-NOM (mg/L C)	Clayey Sediment						Sandy Sediment					
	pH 3.9		pH 5.3		pH 6.7		pH 3.9		pH 5.3		pH 6.7	
	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.
0	45	8	9020	3526	15218	5967	47	7	1168	1159	14602	20072
10	37	0	28787	12	23159	1194	65	11	3096	3094	22121	2812
30	40	4	27609	1686	20135	1252	97	38	641	52	516	53
100	47	4	6882	5606	4583	192	59	4	49	5	33	3
300	67	22	252	92	127	2	15	0	11	2	10	0
Avg	47.1		14510.0		12644.4		56.5		993.4		7456.5	
Stdev	11.6		12913.3		9936.8		29.6		1268.1		10305.9	

5.3.6 Tetravalent Cation Sorption

Tetravalent cation radionuclides of interest to the LLW-PA are Pa^{4+}, Pu^{4+}, Th^{4+}, and Zr^{4+} (Table 1). There were two tetravalent cations included in this study, Th^{4+}, and Zr^{4+}. Thorium is expected to be a good chemical analogue for Pa^{4+} and Pu^{4+}, because all three elements are actinides. Plutonium exists in four oxidation states, +3, +4, +5, and +6, of which +4 and +5 are the most common in the SRS environment (Kaplan and Wilhite 2001). It is important to note that Th^{4+} is expected to be a reasonable analogue for only Pu^{4+} and not for Pu when it exists in the other oxidation states.

With the type of sorption tests conducted for this study, it is impossible to discern the sorption mechanism, i.e., it is impossible to differentiate between chemosorption, adsorption, and precipitation. However, it is readily apparent based on the no-sediment control data presented in section 5.3.2 that precipitation of the tetravalent cations occurred during this study, especially of Th. Consequently, much of the reported sorption can be attributed to the homogeneous (aqueous phase only system) precipitation. Zirconium K_d values followed similar trends as discussed for Ni, Sr (sandy sediment only), Ce, and Eu K_d values (Figure 15 and Table 10). These trends are discussed in Section 5.3.5. However, there are two K_d values with extremely large error bars, perhaps outliers, in the sandy sediment data set, that do not follow the expected trends.

Thorium K_d values followed expected trends (Table 11 and Figure 16). Two slight differences in these trends are:

- Th K_d values in the clayey sediment and in the presence of SR-NOM never decreased below those values measured in system that did not receive any SR-NOM.
- pH did not have a strong impact on Th K_d values, especially in the sandy sediment.

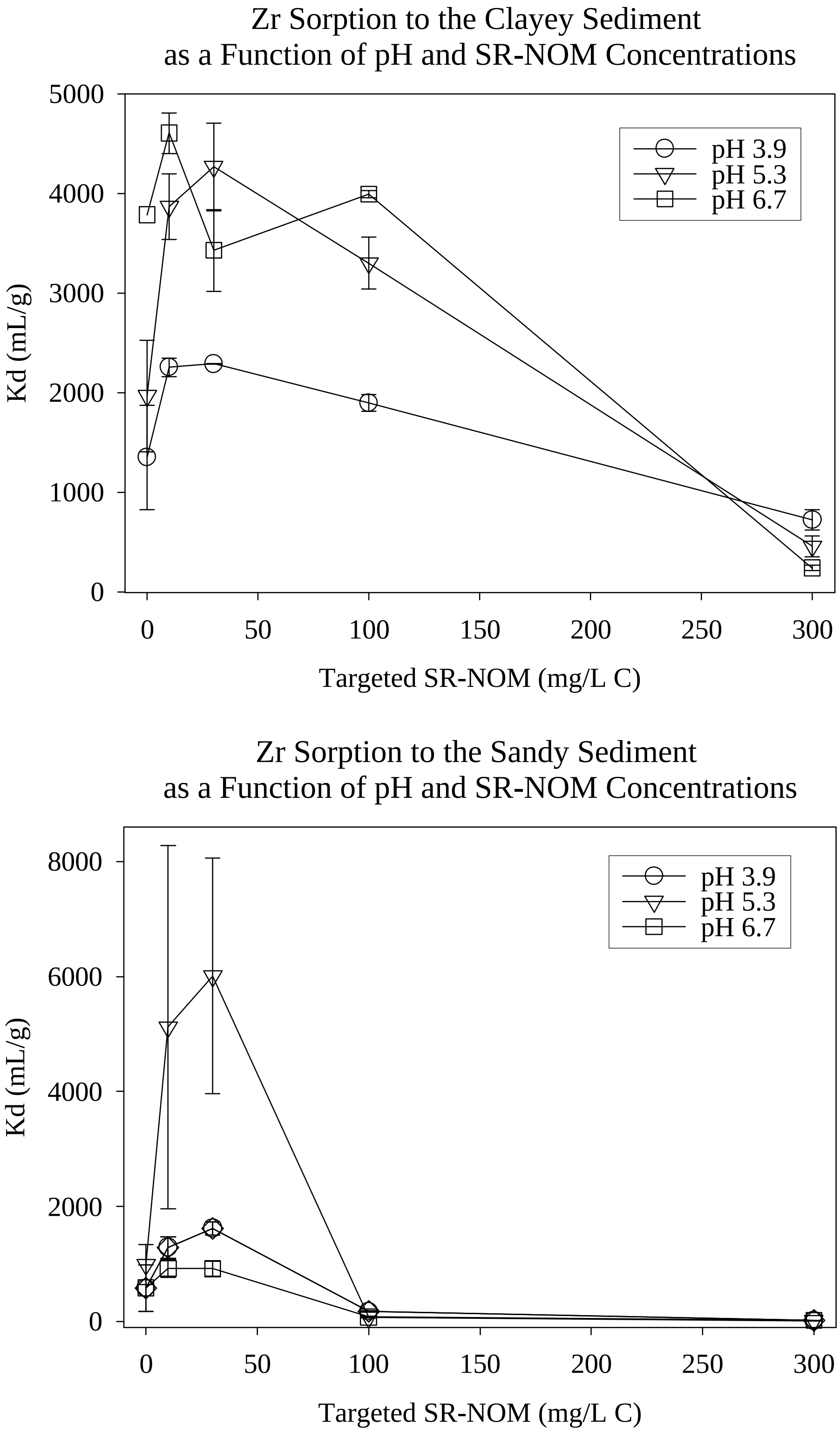
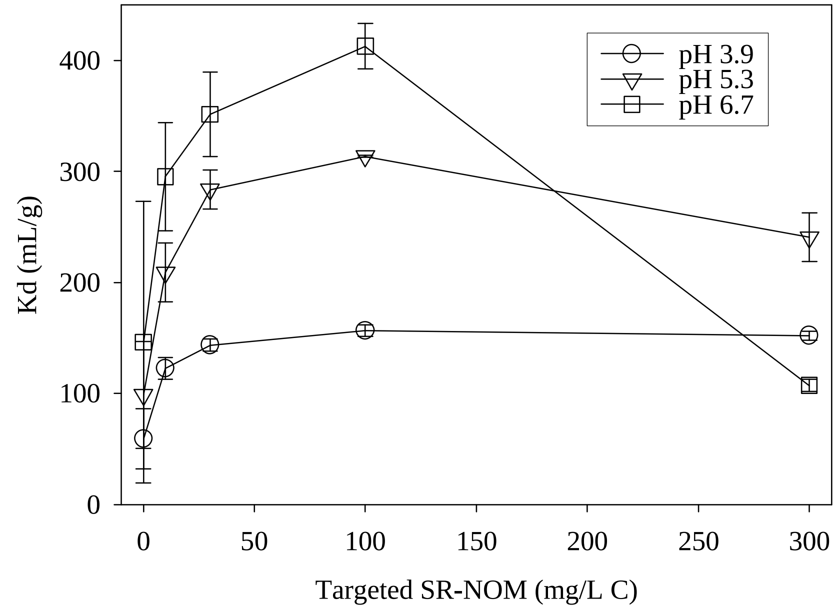


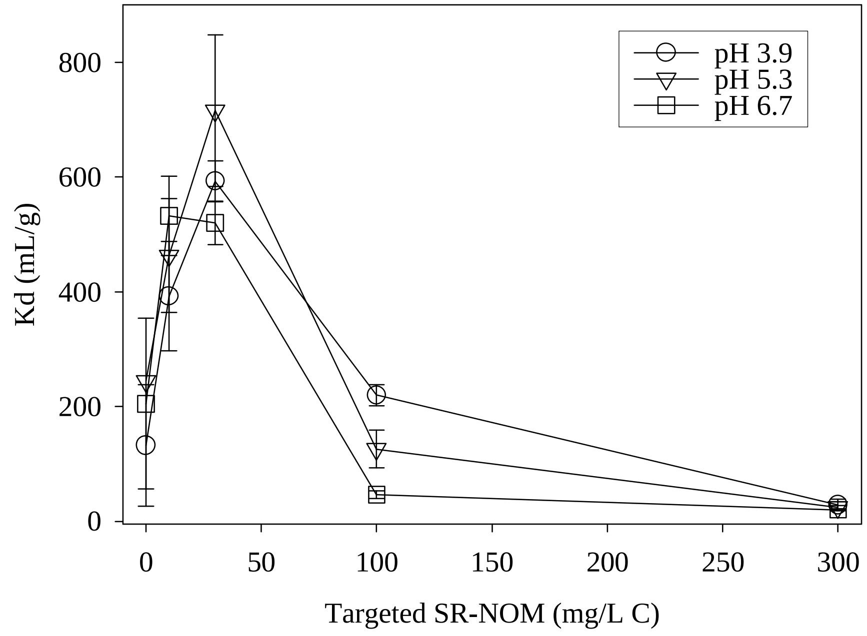
Figure 15. Zr K_d values as a function of pH and SR-NOM concentrations in clayey (top) and sandy (bottom) sediments.

Table 10. Zr K_d values (mL/g).

Target SR-NOM (mg/L C)	Clayey Sediment						Sandy Sediment					
	pH 3.9		pH 5.3		pH 6.7		pH 3.9		pH 5.3		pH 6.7	
	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.
0	1351	526	1969	561	3787	0	580	406	991	352	585	0
10	2256	92	3867	329	4607	2040	1290	187	5122	3161	922	155
30	2290	5	4267	439	3429	409	1620	113	6011	2051	919	133
100	1899	83	3302	262	3993	36	174	10	75	18	79	8
300	724	101	459	106	243	26	16	6	13	2	20	3
Avg.	1704		2773		3212		736		2442		505	
Stdev.	665		1558		1714		698		2895		438	



Th Sorption to the Clayey Sediment
as a Function of pH and SR-NOM Concentrations



Th Sorption to the Sandy Sediment
as a Function of pH and SR-NOM Concentrations

Figure 16. Th K_d values as a function of pH and SR-NOM concentrations in clayey (top) and sandy (bottom) sediments.

Table 11. Th K_d values (mL/g).

Target SR-NOM	Clayey Sediment						Sandy Sediment					
(mg/L C)	pH 3.9		pH 5.3		pH 6.7		pH 3.9		pH 5.3		pH 6.7	
	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.	Avg.	Stdev.
0	59	27	99	48	146	127	132	106	245	0	205	149
10	122	10	209	27	295	49	392	95	463	99	532	69
30	144	5	284	17	351	38	593	36	716	132	520	38
100	157	5	314	1	413	21	220	19	126	33	47	7
300	152	4	241	22	107	6	29	10	24	3	20	2
Avg	127		229		263		273		315		265	
Stdev	40		83		132		223		277		249	

6.0 CONCLUSIONS

6.1 Recommended Conservative CDP-Impacted K_d Values

The approach used to estimate Recommended Conservative (with respect to the Groundwater pathway; low values) CDP-Impacted K_d Values is as follows.

1. A K_d vs. CDP concentration table was created based on the sandy sediment sorption data. The data from the sandy sediment was selected instead of those from the clayey sediment because the latter were typically 2 to 3 times more than the former. The pH 5.3 K_d data was selected as the basis for the look-up table for the 0, 10, 20, and 100 mg/L C K_d values because this pH is closest to the anticipated background pH value at the E-Area subsurface environment, pH 5.5 (Kaplan 2004). pH 3.9 K_d data were used for the 222 mg/L C condition because elevated DOC levels commonly cause sediment pH to decrease. For example Serkiz (2000) used the same sandy sediment employed in this study and observed that at 1 mg/L C from SR-NOM that the pH was 5.5; at 30 mg/L C, the pH was 5.0; and at 1000 mg/L C, the pH was 4.5.
2. Using the K_d data table created in Step 1, CDP Correction Factors were created. These Correction Factors are the ratio of the K_d measured at a given DOC system divided by the K_d when DOC = 0 mg/L C. For example, the CDP Correction Factor for Sr in porewater containing 95 mg/L C is: $\text{Sr-Kd}_{95\text{ ppm C}}/\text{Sr-Kd}_{0\text{ ppm C}}$.
3. CDP Correction Factors were then adjusted in a manner so as to assume that DOC did not enhance radionuclide sorption to sediments. DOC was assumed to have either no effect or it decreased radionuclide sorption. To capture these conservative assumptions, all Correction Factors established in Step 2, that were >1 were reassigned a value of 1. All CDP Correction Factors ≤1 were not adjusted. This was assumed because the length of time that the CDPs would be present in a subsurface system before natural degradation occurred (such as by microbial degradation) is not known.
4. The most recent recommended radionuclide soil K_d values for the LLW-PA were then multiplied by the CDP Correction Factors derived in Step 3 to yield the recommended Conservative CDP-Impacted K_d Values.
5. Finally, the Conservative CDP-Impacted K_d Values were compared to previous values (Serkiz 2000).

As discussed for Step 1 above, measured K_d values as a function of DOC concentration for the sandy sediment at pH 5.3 are presented in Table 12. It is important to keep in mind that the DOC concentrations shown in Table 12 are those that were originally included in the spike concentrations (i.e., total DOC added to the system), and not solution concentrations at the end of the equilibrium period with the sediment. Equilibrium DOC values will be used to model organic carbon sorption, but are not as easy to display. Also presented in Table 12 are the CDP Correction Factors, as discussed in Step 2 above. The trends in this data are consistent:

- K_d values of monovalent and divalent cations gradually increased as DOC concentrations increased, whereas

- K_d values of trivalent and tetravalent cations increased in the presence of low DOC additions, and decreased at elevated DOC additions. In the highest DOC treatments, the tri- and tetra-valent K_d values were less than those measured in treatment that did not receive any DOC.

Table 13 presents the most recently used soil K_d values for the radionuclides of interest to the LLW-PA. The CDP Correction Factors adjusted to assume that the presence of CDP does not enhance radionuclide sorption are presented in Table 14, as described for Steps 3 and 4 on page 45.

Finally, a comparison of past recommended K_d values in Serkiz (2000) with those from this study are presented in Table 15. Serkiz (2000) estimated the K_d values of multivalent radionuclides based on trends observed from CDP laboratory sorption experiments with U and Eu. Furthermore, he assumed that monovalent cationic radionuclides were influenced indirectly by CDPs' influence on pH, not by direct organic matter/cation complexation. This assumption is based on the well established observation that monovalent cations form weak complexes to DOC and that increases in DOC result in decreases in sediment pH. Specifically, monovalent cation K_d values were assigned based on trends observed with Cs^+ sorption to SRS sediments as a function of pH (Johnson 1995). This indirect approach was adopted in the absence of more direct data.

As identified in Table 15 through the use of gray shading, the Recommended CDP-Corrected K_d Values from this report were equal to or greater than those proposed by Serkiz (2000). In the case of most tri- and tetra-valent cations, the differences between the two sets of K_d values were often greater than an order of magnitude. The main reasons for these differences can in part be attributed to the differences in assumptions in developing these two data sets and the need for greater conservatism by Serkiz (2000) in the absence of appropriate data.

6.2 Utilization of Recommended CDP-Impacted K_d Values in Future PA Modeling

Incorporation of recommended CDP-Impacted K_d Values into future PA modeling will be the subject of a follow-up project. The general approach will be to first run an organic carbon sorption model in the transport code to estimate spatial distributions of DOC (a measure of CDP) in the aqueous phase. This sorption model will likely not be linear, i.e., it will not be well described by a single K_d value, because of the wide range of organic carbon concentrations expected in the system. Instead, a more robust model, applicable over a wide range of DOC concentrations will need to be invoked, such as a Freundlich or a model in which surface electrostatic properties are taken into consideration, such as one of the many surface complexation models. Once the dissolved organic carbon or sorbed organic carbon concentrations are established, then the K_d values recommended in Table 15 will be incorporated in a radionuclide simulation. The final recommended CDP-impacted K_d values may be organized as a function of pH and DOC concentrations, instead of only by DOC as presented in Table 15.

Table 12. CDP Correction Factors based on K_d values measured in the pH 3.9 or 5.3 sandy sediment system.

		K_d (mL/g)					CDP Correction Factors			
	Val-ance	0[(a)] (mg/L C)	10 (mg/L C)	20 (mg/L C)	95 (mg/L C)	222 [(b)] (mg/L C)	$K_d(10)/K_d(0)$	$K_d(20)/K_d(0)$	$K_d(95)/K_d(0)$	$K_d(222)/K_d(0)$
Cs	+1	11.4	13	13	18.9	17	1.14	1.14	1.66	1.49
Ni	+2	6.8	7.7	12.4	9.6	6	1.13	1.82	1.41	0.88
Sr	+2	4.5	5.5	10.7	8.5	2	1.22	2.38	1.89	0.44
Ce	+3	1220	3840	1210	69	21	3.15	0.99	0.057	0.02
Eu	+3	1170	3100	641	49	15	2.65	0.55	0.042	0.01
Ce& Eu	+3						2.900[(c)]	0.770	0.049	0.015
Th	+4	245	463	716	126	29	1.89	2.92	0.514	0.12
Zr	+4	990	5120	6010	75	16	5.17	6.07	0.076	0.02

[(a)] DOC concentration represent those in the aqueous phase prior to coming into contact with sediment, i.e., the leachate DOC concentrations rather than the final concentrations after the system obtains steady state with the sediment.

[(b)] pH 3.9 K_d data was used for the 222 mg/L C condition because elevated DOC levels commonly cause sediment pH to decrease. For example Johnson (1995) used the same sandy sediment as used in this study and observed that at 1 mg/L C from SR-NOM that the pH was 5.5; 30 mg/L C, the pH was 5.0, at 1000 mg/L C, the pH was 4.5.

[(c)] Ce & Eu average CDP Correction Factors.

Table 13. Present soil Kd values for radionuclides of interest to the LLW-PA.

Radionuclide	Assumed Valance	Analogue	Present Soil K_d Values	Ref.[a]
Ac	3	Ce & Eu	450	1
Am	3	Ce & Eu	1900	1
C[a]	-2	None	2	1
Cf	3	Ce & Eu	510	1
Cm	3	Ce & Eu	4000	1
Cs	1	Cs	18	2
Eu	3	Eu	7300	2
H[a]	1	None	0	1
I	-1	None	0.6	1
Nb	-1	None	160	1
Ni	2	Ni	400	1
Np	1	Cs	5	1
Pa	4	Th	550	1
Pb	2	Ni	270	1
Pd	2	Ni	55	1
Po	2	Ni	150	1
Pu	4	Th	370	3
Ra	2	Sr	500	1
Rb	1	Cs	55	1
Se	-1	None	36	3
Sn	2	Ni	130	1
Sr	2	Sr	10	1
Tc	-1	None	0.36	1
Th	4	Th	3200	1
U	2	Sr	800	2
Zr	4	Zr	600	1

[a] References: 1 = McDowell-Boyer et al. 2000; 2 = Serkiz 2000; 3 = Kaplan 2004

Table 14. CDP Correction Factors assuming no enhanced sorption due to presence of CDP and CDP-Corrected Kd values.

Radio-nuclide	Present Soil K_ds(a)	CDP Correction Factors Assuming No Enhanced Sorption in the Presence of DOC				CDP Corrected Kd (mL/g)			
	(mL/g)	10 mg/L C	20 mg/L C	95 mg/L C	222 mg L C	10 mg/L C	20 mg/L C	95 mg/L C	222 mg/L C
Ac	450	1.00	0.770	0.049	0.015	450	347	22	7
Am	1900	1.00	0.770	0.049	0.015	1900	1464	94	29
C(b)	2								
Cf	510	1.00	0.770	0.049	0.015	510	393	25	8
Cm	4000	1.00	0.770	0.049	0.015	4000	3081	197	60
Cs	18	1.00	1.00	1.00	1.00	18	18	18	18
Eu	7300	1.00	0.55	0.04	0.01	7300	4006	306	94
H(b)	0								
I(b)	0.6								
Nb	160								
Ni	400	1.00	1.00	1.00	0.88	400	400	400	353
Np	5	1.00	1.00	1.00	1.00	5	5	5	5
Pa	550	1.00	1.00	0.51	0.12	550	550	283	65
Pb	270	1.00	1.00	1.00	0.88	270	270	270	238
Pd	55	1.00	1.00	1.00	0.88	55	55	55	49
Po	150	1.00	1.00	1.00	0.88	150	150	150	132
Pu	370	1.00	1.00	0.51	0.12	370	370	190	44
Ra	500	1.00	1.00	1.00	0.44	500	500	500	222
Rb	55	1.00	1.00	1.00	1.00	55	55	55	55
Se	36								
Sn	130	1.00	1.00	1.00	0.88	130	130	130	115
Sr	10	1.00	1.00	1.00	0.44	10	10	10	4
Tc	0.36								
Th	3200	1.00	1.00	0.51	0.12	3200	3200	1646	379
U	800	1.00	1.00	1.00	0.44	800	800	800	356
Zr	600	1.00	1.00	0.08	0.02	600	600	45	10

(a) References for most recent Soil Kd values are presented in Table 13.

(b) No analogues were included in this study for C, H, I, Se, and Tc.

Table 15. Comparison of Recommended CDP-Corrected K_d Values from this study and those proposed by Serkiz (2000); larger K_d values based on comparison of both sets of data are shaded.

	Recommended CDP-Corrected K_d Values (mL/g)					Serkiz (2000) SDP-Corrected K_d Values (mL/g)				
Radio-nuclide	<1 mg/L C (a)	1 to 10 mg/L C	10 to 20 mg/L C	20 to 100 mg/L C	>225 mg L C	<1 mg/L C (a)	1 to 10 mg/L C	10 to 30 mg/L C	30 to 100 mg/L C	100 to 1000 mg/L C
Ac	450	450	347	22	7	450	80	13	4	2
Am	1900	1900	1464	94	29	1900	338	55	18	10
C(b)	2	2	2	2	2	2	2	2	2	2
Cf	510	510	393	25	8	510	91	15	5	3
Cm	4000	4000	3081	197	60	4000	712	115	38	22
Cs	18	18	18	18	18	18	12	5	5	5
Eu	7300	7300	4006	306	94	7300	1300	210	70	40
H(b)	0	0	0	0	0	0	0	0	0	0
I(b)	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Nb	160	160	160	160	160	160	160	160	160	160
Ni	400	400	400	400	353	400	163	8	3.8	2.2
Np	5	5	5	5	5	5	3	1	1	1
Pa	550	550	550	283	65	550	3	1.4	1.4	1.4
Pb	270	270	270	270	238	270	110	5	3	1
Pd	55	55	55	55	49	55	22	1.1	0.5	0.3
Po(b)	150	150	150	150	132	150	150	150	150	150
Pu	370(d)	370	370	190	44	100	18	3	1	1
Ra	500	500	500	500	222	500	203	10	4.8	2.7
Rb(b)	55	55	55	55	55	55	3	1	1	1
Se	36(d)	36	36	36	36	5	5	5	5	5
Sn	130	130	130	130	115	130	53	2.6	1.3	0.7
Sr	10	10	10	10	4	10	4	0.2	0.1	0.1
Tc(b)	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36
Th	3200	3200	3200	1646	379	3200	570	92	31	18
U(c)	800	325	16	8	4	800	325	16	8	4
Zr	600	600	600	45	10	600	107	17	6	3

(a) Column two contains the Most Recent Soil K_d values. Column seven contains the most recent soil K_d values in the year 2000.

(b) Anion K_d values recommended in this study and in Serkiz (2000), were assumed not to be influenced by the presence of CDP.

(c) U K_d values recommended in this study are adopted from Serkiz 2000, since the later were based on actual laboratory studies with U and SR-NOM.

(d) Pu and Se soil K_d values were increased during the interim between issuing Serkiz (2000) and this report.

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8.0 APPENDIX A: DETAILED DESCRIPTION OF MATERIALS AND METHODS

Detailed Work Instructions for Influence of DOC on Constituent of Concern Sorption to SRS Sediments

Dan Kaplan & Steve Serkiz
5/24/04

Objective: The overall objective of this study is to create input geochemistry values for PA calculations related to constituents of concern (COC) sorption to E-Area sediment in the presence of cellulose degradation products (CDP). The specific objectives are to:

1. create a soil titration,
2. determine how pH varies as a function of SR-NOM (FA; an analog for CDP) concentrations,
3. determine how SR-NOM sorbs to E-Area sediment as a function of pH, and
4. determine sorption envelopes (sorption vs. pH) of COCs as a function of SR-NOM concentrations.

General Approach: The general approach is to incrementally add complexity to the same set of tubes. The first system will include a pH adjusted soil + water system (Figure 1). This will generate sediment titration curves (Objective 1). SR-NOM will then be added to the pH-adjusted sediments, the system will be permitted to come to equilibrium and then pH and FA concentrations will be measured. This will provide SR-NOM sorption isotherms as a function of 3 pH levels (Objective 3) and the relationship between FA vs. pH (Objective 2). Finally, COCs will be added to the sediment + water + FA system. After 1 week, COC concentrations will be measured. This will provide a series of COC vs. FA and COC vs. pH Kd values. To lower costs, there will be a down selection of pH levels evaluated: starting at 11 pH levels in the "sediment + water system" and then 3 pH levels for the "sediment + water + FA system" and the "sediment + water + FA + COC system". Five FA concentrations were used 0, 10, 30, 100, and 300 mg L^{-1} C.

Materials:

1. 200 50-mL centrifuge tubes
2. BG1 sandy sediment
3. subsurface clayey sediment
4. 2.0-L 0.02 M NaCl
5. 0.1-L 0.005 M HCl
6. 0.1-L 0.005 M NaOH
7. 0.1-L 0.05 M HCl
8. 0.1-L 0.05 M NaOH
9. <u>75-mL 10,000 mg/L SR-NOM Stock</u>: dissolve 0.75g IHSS SR-NOM (FA; Suwannee River SR-NOM) in 75mL water. Mix well. Store in refrigerator and in light-proof or amber glass container.
10. <u>70-mL 1000 mg/L SR-NOM Stock</u>: Add 7 mL of 10,000 mg/L FA Stock solution to a 25 mL volumetric flask. Bring up to volume with DI water. Mix well. Store in refrigerator and in light-proof or amber glass container.
11. ICP-MS standards stock solution (Dan will acquire)

12. ~100 24-mL glass vials: Borosilicate glass, with PTFE-lined screw cap.
13. 0.5% HNO_3: Add 5 mL of HNO_3 to 995mL water.
14. 100 acid washed scintillation vials
15. 100 water-washed 0.45-µm filters

Methods:

Scoping Sediment-Water Experiment:

1. Label tubes as shown in Table 1 and record tare weights.
2. Add 5 g of appropriate sediment to treatment tubes. Record "tare + sediment" weight in Table 1.
3. Add acid, base, ionic strength salt and distilled water as shown in Table 1. Record final weight in Table 1.
4. Place tubes on an air tight box and leave on platform shaker for ~1 week.
5. Measure pH and enter into Table 1.
6. Select 3 pH treatments for the clayey sediment and another 4 pH treatments for the sandy sediment to provide a good titration curves. These tubes will constitute the 0-ppm FA treatment in the Sediment + Water + FA study.

Sediment-Water-FA Experiment:

[For the Sand, tubes # 4, 8, & 9 were selected. For the Clay, tubes # 3, 10, & 11 were selected.]

Preparation of Additional Sets of pH-adjusted Sediments Samples

7. Prepare 8 additional sets of tubes as shown in Table 2: 2 sets for 10-ppm DOC, 2 sets for 30-ppm DOC, 2 sets for 100-ppm DOC, and 2 sets for 300-ppm DOC.
8. Follow steps 1 – 4, except use the labeling presented in Table 2 and record data in Table 2. Let samples equilibrate on a shaker for the same duration as used in Step 4. Note: You do not need to measure pH at the end of the equilibration period as was done for Step 5.
9. Remove 3-mL from each tube described in Table 2. We're doing this to ensure we have enough volume in tube for subsequent acid, base, FA, and COC solution additions.

Preparation of No-Sediment Control Samples

10. Label tubes as shown in Table 3. Record "Tare Wt." in Table 3. Add 40-mL of 0.02 M NaCl.

Adding FA

11. Add 0, 1, or 3 mL of appropriate FA stock solution to each tube as shown in Tables 2 & 3.
12. Put samples in light-proof box and place box in refrigerator for overnight.
13. Take samples out of refrigerator and let tubes come to near room temperature. pH adjust solutions by adding 0.01 M NaOH, 0.01 M HCl, 0.1 M NaOH 0.1 M HCl, and/or 1.0 M NaOH (NaOH solutions will be needed more than HCl solutions) to the targeted pH levels listed in Tables 2 & 3. We want to add <~2 mL of acid or base. Please ask Carl, Dave or Adrian to help you because we need to complete all the pH adjustments in 1 or 2 days.

14. Return samples to the light-proof box and refrigerator.
15. Shake samples at the start and end of each work shift. Assign someone to shake tubes on Friday.
16. After one week, take tubes out of refrigerator and let tubes come to near room temperature. pH adjust tubes again. (Again, request help from Carl, Dave or Adrian. We need to complete this step in 1 or 2 days.)
17. Measure weight of each tube and contents and record "Wt after adj pH of FA soln wt (g)" in Tables 2 & 3. Show me these weights and we'll decide what weight to target for the next step, which is to bring all the tubes up to the same weight.
18. Record in Tables 2 & 3 the amount of water needed to bring each tube up to the same volume. Add water to tubes.
19. Put tubes back in light-proof box and the box in a refrigerator.

Sediment-Water-DOC-COC Experiment:

20. Add 0.25-mL of Ni, Sr, K, Cs, Eu, Ce, Th, and Zr of 100 ppm ICP-MS standards solution to each tube.
21. Add 0.75 mL of Th 10 ppm ICP-MS standards solution to each tube.
22. Put tubes back in light-proof box and the box in a refrigerator. Shake box vigorously 2 times a day for 1 week.
23. After one week, take tubes out of refrigerator and let tubes come to near room temperature. Measure pH and record in Tables 2 & 3.
24. Let sediment settle to bottom of tube or if necessary, centrifuge (also it is OK to centrifuge some but not all samples).
25. Pass >28 mL of each sample through washed 0.45-µm filter (see instruction in Materials section on how to wash filters; Steve will provide). Collect filtrate in acid washed 50-mL centrifuge tubes.
26. Add 0.150 mL of concentrated Ultra Pure HNO_3 to each filtered aqueous sample to preserve the aqueous samples. (Assuming 30-mL of sample solution, this is a 0.5%-HNO_3 addition.)
27. Each sample will then be pipetted into 3 containers (2 24-mL glass vials for duplicate C analyses and 1 acid washed scintillation vial for ICP-MS)
    - 10.0 mL into a 24 mL glass vial (labeled e.g., 900-I, 901-I, 902-I, 903-I…). These are replicate 1 for DOC measurements.
    - 10.0 mL into a 24 mL glass vial (labeled e.g., 900-II, 901-II, 902-II, 903-II…). These are replicate 2 for DOC measurements.
    - The remainder of sample, >8mL, into the acid washed scintillation vials (labeled identically to samples, e.g., 900, 901, 902, 903, 904… These samples will be used to measure ICP-MS at UGa and will be used to measure absorbance on the spectrophotometer.
28. Add 10.0 mL of 0.5% HNO_3 (995 mL water + 5 mL HNO_3) to each 24mL vial.
29. Store all samples in dark and in refrigerator.
30. The samples in the acid washed scintillation vials will be used to measure absorbance on the spectrophotometer prior to shipping to UGa. Anna will help us with this step.
31. Submit samples to UGa for ICP-MS analysis and to Steve for DOC analysis.

Order-of-Addition Controls: *(These Controls are design to determine whether the order in which we add the FA and COC has an effect on how much metal sorption we measure. There are actually two sets of controls, the first set of controls are described in steps 32 – 44, and the second set of controls are described in steps 45 – 56.)*

32. First set of Order-of-Addition Controls: Label 4 50-mL centrifuge tubes as shown in the top 4 rows in Table 4. Record “tare wt”.
33. Add 5 g surface clayey sediment to each tube.
34. Add 40-mL of 0.02 M NaCl. pH-adjust to the pH shown in Table 4 using NaOH or HCl. Put in refrigerator for week. Agitate twice a day.
35. Add COCs as done in steps 20 and 21 (0.25 mL of mixed spike and 0.75 mL of Th spike). Put in refrigerator for ~two days. Agitate twice a day.
36. Add 0.4 mL of 10,000 mg/L SR-NOM Stock to each tube.
37. pH-adjust using NaOH or HCl.
38. Weigh and record “tare+ sed+COC+FA wt”.
39. See me and we’ll decide how much water to add to each tube to make similar total volumes.
40. Add appropriate amount of water (Table 4).
41. Put tubes in light-proof box and box put in refrigerator. Shake sample twice a day for one week.
42. Pass ~10 mL of each sample through washed 0.45-µm filter and store in labeled acid wash scintillation vial.
43. Add 0.05 mL (50-µL) of concentrated Ultra Pure HNO_3 to each filtered aqueous sample to preserve the aqueous samples (this is a 0.5%-HNO_3 addition).
44. Send to UGa for ICP-MS.
45. Second set of Order of Addition Controls: Label 4 50-mL centrifuge tubes as shown in the bottom 4 rows in Table 4. Record “tare wt”. Add 40-mL of 0.02 M NaCl. pH-adjust using NaOH or HCl. Put in refrigerator for week. Agitate twice a day.
46. Add 1.25 mL of mixed COC solution + 3.75 mL of Th spike solution + 2.0 mL of 10,000 mg/L SR-NOM Stock + 2.0 mL of 1,000 mg/L SR-NOM Stock to a small vial (such as a scintillation vial). Mix on platform shaker for 30 minutes.
47. Add 1.8 mL of above mixture described in Step 46 to each tube.
48. pH-adjust using NaOH or HCl.
49. Put in refrigerator for week. Agitate twice a day.
50. Add 5 g surface clayey sediment to each tube.
51. pH-adjust using NaOH or HCl.
52. Record “tare+FA+COC+sed wt”.
53. See me and we’ll decide how much water to add to each tube to make similar total volumes.
54. Add appropriate amount of water (see Table 4).
55. Put tubes in light-proof box and box put in refrigerator. Shake sample twice a day for one week.
56. Follow steps 42 – 44.

Safety Topics to Discuss: Non-rad. Weak acids and weak bases. ICP-MS stock solution. Centrifuge.

Waste: Depending on the final list and concentration of COCs, it may be possible to dispose of all waste as non-hazardous. Cl will not be an issue. Concentrated stock solutions of COCs (ICP-MS Standards Solution) will not be thrown out.

Hazards Analysis Checklist: It is located in WSRC-NB-2003-00251 on page 11.

Table 1. Sample ID and amount of acid base, ionic strength salt and distilled water needed for each sample.

Sample ID (pH#-FA-Rep-Sed)	pH tube #	Sed-iment	mL 0.005M HCl	mL 0.005 M NaOH	mL 0.02 M NaCl	mL H_2O	pH after 1 wk	Tare wt (g)	Tare + Sed. Wt. (g)
1-0-1-C	1	Clay	25	0	18.8	6.2	3.13	11.741	16.745
1-0-2-C	1	Clay	25	0	18.8	6.2	3.12	11.828	16.828
2-0-1-C	2	Clay	15	0	21.2	13.8	3.50	11.715	16.719
2-0-2-C	2	Clay	15	0	21.2	13.8	3.49	11.755	16.759
3-0-1-C	3	Clay	4	0	24	22	4.18	11.770	16.770
3-0-2-C	3	Clay	4	0	24	22	4.16	11.738	16.737
4-0-1-C	4	Clay	2	0	24.5	23.5	4.36	11.714	16.716
4-0-2-C	4	Clay	2	0	24.5	23.5	4.36	11.777	16.778
5-0-1-C	5	Clay	0.5	0	24.8	24.7	4.49	11.744	16.746
5-0-2-C	5	Clay	0.5	0	24.8	24.7	4.48	11.794	16.792
6-0-1-C	6	Clay	0	0	25	25	4.53	11.728	16.728
6-0-2-C	6	Clay	0	0	25	25	4.53	11.821	16.821
7-0-1-C	7	Clay	0	0.5	24.8	24.7	4.59	11.847	16.846
7-0-2-C	7	Clay	0	0.5	24.8	24.7	4.59	11.735	16.737
8-0-1-C	8	Clay	0	2	24.5	23.5	4.75	11.780	16.778
8-0-2-C	8	Clay	0	2	24.5	23.5	4.75	11.804	16.804
9-0-1-C	9	Clay	0	4	24	22	4.93	11.738	16.739
9-0-2-C	9	Clay	0	4	24	22	4.94	11.776	16.777
10-0-1-C	10	Clay	0	15	21.2	13.8	6.08	11.721	16.721
10-0-2-C	10	Clay	0	15	21.2	13.8	6.06	11.744	16.746
11-0-1-C	11	Clay	0	25	18.8	6.2	8.72	11.730	16.734
11-0-2-C	11	Clay	0	25	18.8	6.2	8.74	11.715	16.720
1-0-1-S	1	Sand	25	0	18.8	6.2	2.79	11.709	16.712
1-0-2-S	1	Sand	25	0	18.8	6.2	2.78	11.755	16.756
2-0-1-S	2	Sand	15	0	21.2	13.8	3.02	11.702	16.706
2-0-2-S	2	Sand	15	0	21.2	13.8	3.03	11.736	16.739
3-0-1-S	3	Sand	4	0	24	22	3.74	11.703	16.705
3-0-2-S	3	Sand	4	0	24	22	3.76	11.711	16.714
4-0-1-S	4	Sand	2	0	24.5	23.5	4.11	11.824	16.825
4-0-2-S	4	Sand	2	0	24.5	23.5	4.11	11.737	16.738
5-0-1-S	5	Sand	0.5	0	24.8	24.7	4.53	11.721	16.721
5-0-2-S	5	Sand	0.5	0	24.8	24.7	4.54	11.701	16.701
6-0-1-S	6	Sand	0	0	25	25	4.71	11.842	16.844
6-0-2-S	6	Sand	0	0	25	25	4.73	11.703	16.704
7-0-1-S	7	Sand	0	0.5	24.8	24.7	4.96	11.726	16.726
7-0-2-S	7	Sand	0	0.5	24.8	24.7	4.95	11.705	16.706
8-0-1-S	8	Sand	0	2	24.5	23.5	5.53	11.764	16.767
8-0-2-S	8	Sand	0	2	24.5	23.5	5.51	11.719	16.722
9-0-1-S	9	Sand	0	4	24	22	7.24	11.698	16.698
9-0-2-S	9	Sand	0	4	24	22	7.37	11.728	16.729
10-0-1-S	10	Sand	0	15	21.2	13.8	10.54	11.698	16.699
10-0-2-S	10	Sand	0	15	21.2	13.8	10.54	11.819	16.823
11-0-1-S	11	Sand	0	25	18.8	6.2	10.91	11.727	16.729
11-0-2-S	11	Sand	0	25	18.8	6.2	10.91	11.754	16.754

Table 2. Addition of SR-NOM to pH adjusted tubes containing sediment.

Sample ID (pH #-FA-Rep-Sed)	**Lab ID**	**Sed.**	**Target pH (±0.15)**	**SR-NOM (ppmC)**	**0.005 M HCl (mL)**	**0.005 M NaOH (mL)**	**0.02 M NaCl**	**H_2O (mL)**	**Tare wt (g)**	**Tare + Sed. wt. (g)**	**FA added (mL-Stock ppm FA)**	**Wt after adj pH of FA soln wt (g)**	**Amt water added (g)**	**Final pH (pH)**
Proc. Step					**8**	**8**	**8**	**8**	**8**	**8**	**11**	**17**	**18**	**23**
3-0-1-C	901	Clay	4.0	0	4	0	24	22	11.770	16.770	0	*		
3-0-2-C	902			0					11.738	16.737	0	*		
3-10-1-C	903			10							1-1,000	*		
3-10-2-C	904			10							1-1,000			
3-30-1-C	905			30							3-1,000			
3-30-2-C	906			30							3-1,000			
3-100-1-C	907			100							1-10,000			
3-100-2-C	908			100							1-10,000			
3-300-1-C	909			300							3-10,000			
3-300-2-C	910			300							3-10,000			
10-0-1-C	911		6.1	0	0	15	21.2	13.8	11.721	16.721	0			
10-0-2-C	912			0					11.744	16.746	0			
10-10-1-C	913			10							1-1,000			
10-10-2-C	914			10							1-1,000			
10-30-1-C	915			30							3-1,000			
10-30-2-C	916			30							3-1,000			
10-100-1-C	917			100							1-10,000			
10-100-2-C	918			100							1-10,000			
10-300-1-C	919			300							3-10,000			
10-300-2-C	920			300							3-10,000			
11-0-1-C	921		8.7	0	0	25	18.8	6.2	11.730	16.734	0			
11-0-2-C	922			0					11.715	16.720	0			
11-10-1-C	923			10							1-1,000			
11-10-2-C	924			10							1-1,000			
11-30-1-C	925			30							3-1,000			
11-30-2-C	926			30							3-1,000			
11-100-1-C	927			100							1-10,000			
11-100-2-C	928			100							1-10,000			
11-300-1-C	929			300							3-10,000			
11-300-2-C	930			300							3-10,000			

Table 2 (continuation). Addition of SR-NOM to pH adjusted tubes containing sediment.

Sample ID (pH #-FA-Rep-Sed)	**Lab ID**	**Sed.**	**Target pH (±0.15)**	**SR-NOM (ppmC)**	**0.005 M HCl (mL)**	**0.005 M NaOH (mL)**	**0.02 M NaCl**	**H_2O (mL)**	**Tare wt (g)**	**Tare + Sed. wt. (g)**	**FA added (mL-Stock ppm FA)**	**Wt after adj pH of FA soln wt (g)**	**Amt water added (g)**	**Final pH (pH)**
Proc. Step					**8**	**8**	**8**	**8**	**8**	**8**	**11**	**17**	**18**	**23**
4-0-1-S	931	Sand	4.1	0	2	0	24.5	23.5	11.824	16.825	0			
4-0-2-S	932			0					11.737	16.738	0			
4-10-1-S	933			10							1-1,000			
4-10-2-S	934			10							1-1,000			
4-30-1-S	935			30							3-1,000			
4-30-2-S	936			30							3-1,000			
4-100-1-S	937			100							1-10,000			
4-100-2-S	938			100							1-10,000			
4-300-1-S	939			300							3-10,000			
4-300-2-S	940			300							3-10,000			
8-0-1-S	941		5.5	0	0	2	24.5	23.5	11.764	16.767	0			
8-0-2-S	942			0					11.719	16.722	0			
8-10-1-S	943			10							1-1,000			
8-10-2-S	944			10							1-1,000			
8-30-1-S	945			30							3-1,000			
8-30-2-S	946			30							3-1,000			
8-100-1-S	947			100							1-10,000			
8-100-2-S	948			100							1-10,000			
8-300-1-S	949			300							3-10,000			
8-300-2-S	950			300							3-10,000			
9-0-1-S	951		7.2	0	0	4	24	22	11.698	16.698	0			
9-0-2-S	952			0					11.728	16.729	0			
9-10-1-S	953			10							1-1,000			
9-10-2-S	954			10							1-1,000			
9-30-1-S	955			30							3-1,000			
9-30-2-S	956			30							3-1,000			
9-100-1-S	957			100							1-10,000			
9-100-2-S	958			100							1-10,000			
9-300-1-S	959			300							3-10,000			
9-300-2-S	960			300							3-10,000			

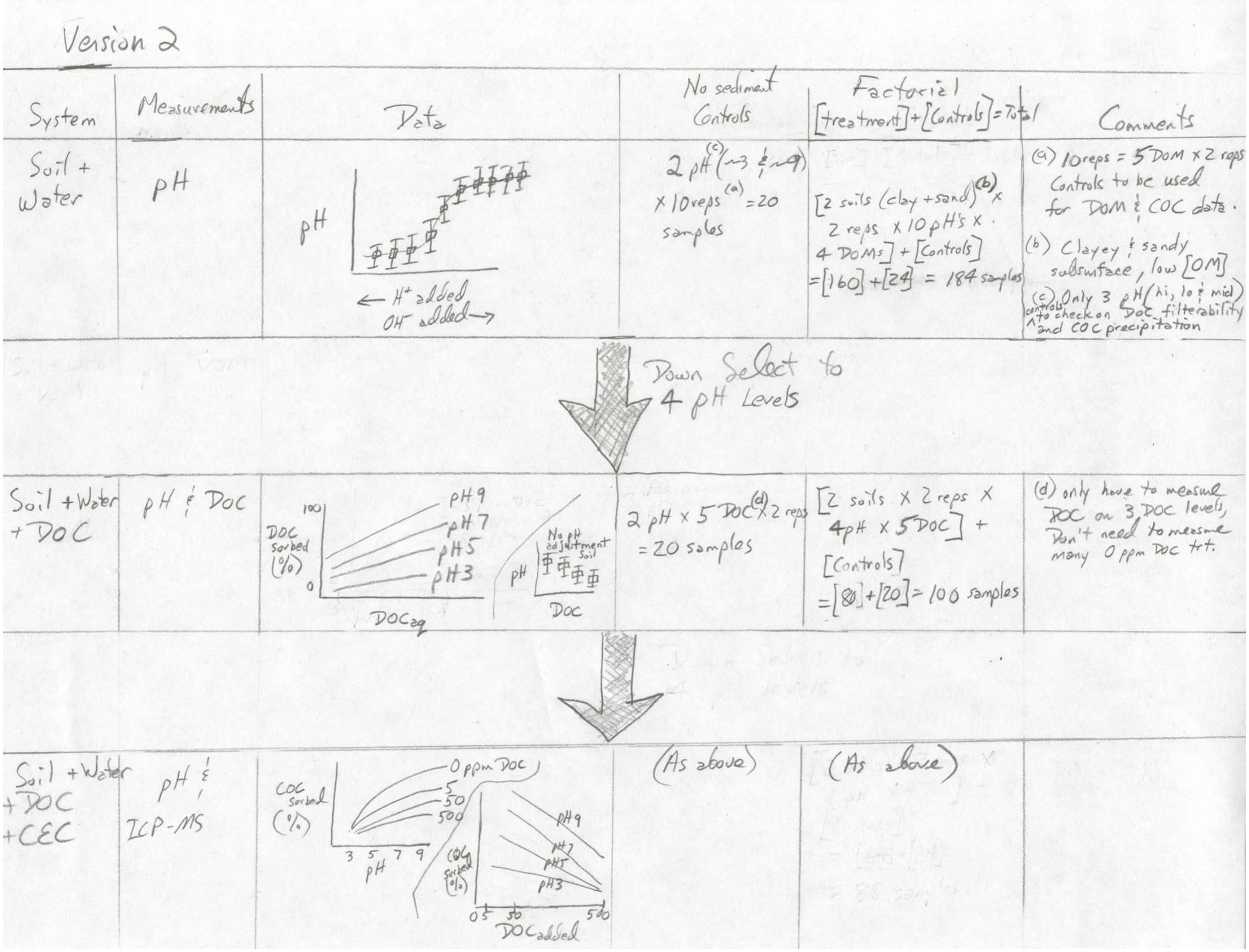
Table 3. Preparation of No-Sediment Control Samples.

Sample ID (pH #-FA-Rep-Sed)	**Lab ID**	**Targeted pH (±0.15)**	**SR-NOM (ppm C)**	**Tare Wt (g)**	**FA added (mL/Stock ppm)**	**Wt after adj pH of FA soln wt (g)**	**Amt water added (g)**	**Final pH (pH)**
Proc. Step				**10**	**11**	**17**	**18**	**22**
4-0-1-N	961	4.1	0		0			
4-0-1-N	962		0		0			
4-10-1-N	963		10		1-1,000			
4-10-1-N	964		10		1-1,000			
4-30-1-N	965		30		3-1,000			
4-30-1-N	966		30		3-1,000			
4-100-1-N	967		100		1-10,000			
4-100-1-N	968		100		1-10,000			
4-300-1-N	969		300		3-10,000			
4-300-1-N	970		300		3-10,000			
8-0-1-N	971	8.0	0		0			
8-0-2-N	972		0		0			
8-10-1-N	973		10		1-1,000			
8-10-1-N	974		10		1-1,000			
8-30-1-N	975		30		3-1,000			
8-30-1-N	976		30		3-1,000			
8-100-1-N	977		100		1-10,000			
8-100-1-N	978		100		1-10,000			
8-300-1-N	979		300		3-10,000			
8-300-1-N	980		300		3-10,000			

Table 4. Preparation of Order-of–Addition Controls (Clayey Sediment & 100 ppm C Only)

Sample ID (pH-FA-Rep-Sed)	**Lab ID**	**Target pH (±0.15)**	**Tare wt. (g)**	**Tare+Sed+COC+FA wt. (g)**	**Make up Water wt. (g)**
Proc. Step			**32**	**38**	**40**
4-100-1-COC/FA	981	4.0			
4-100-2-COC/FA	982	4.0			
8-100-1-COC/FA	983	8.0			
8-100-2-COC/FA	984	8.0			
Proc. Step			**45**	**52**	**54**
4-100-1-COC+FA	985	4.0			
4-100-2-COC+FA	986	4.0			
8-100-1-COC+FA	987	8.0			
8-100-2-COC+FA	988	8.0			

Figure 1. Original conceptualization of Experimen



Version 2

System	Measurements	Data	No sediment Controls	Factorial [treatment]+[Controls]=Total	Comments
Soil + Water	pH	pH ← H+ added OH- added →	2 pH(c) (~3 & ~9) × 10reps(a) = 20 samples	[2 soils (clay + sand)(b) × 2 reps × 10 pH's × 4 DOMs] + [Controls] = [160] + [24] = 184 samples	(a) 10reps = 5 DOM × 2 reps Controls to be used for DOM & COC data. (b) Clayey & sandy subsurface, low [OM] (c) Only 3 pH (hi, lo & mid) controls to check on DOC filterability and COC precipitation
		Down Select to 4 pH Levels			
Soil + Water + DOC	pH & DOC	DOC sorbed (%) 100 0 pH9 pH7 pH5 pH3 DOCaq pH No pH adjustment Soil DOC	2 pH × 5 DOC(d) × 2 reps = 20 samples	[2 soils × 2 reps × 4pH × 5 DOC] + [Controls] = [80] + [20] = 100 samples	(d) only have to measure DOC on 3 DOC levels, Don't need to measure many 0 ppm DOC trt.
Soil + Water + DOC + CEC	pH & ICP-MS	COC sorbed (%) 0 ppm DOC 5 50 500 3 5 7 9 pH COC sorbed (%) pH9 pH7 pH5 pH3 0 5 50 500 DOCadded	(As above)	(As above)	

9.0 APPENDIX B: ADDITIONAL DATA

Table A 1. Point of Zero Salt Effect for Sandy Sediment Raw Data.

g (0.005=	0.925 M	Ionic strengths of background solutions; Corrected by Davies Equation.
g (0.01)=	0.89 M	
g (0.05)=	0.807 M	

Sample	Soil Weight (g)	Blank pH	2 week pH		DH	2 week DOH	DH-DOH
1-005-s	2.5547	2.77	3.74	*	0.001516	-4.90657E-11	6.41647E-05
2-005-s	2.5357	2.93	4.26	*	0.00112	-1.73459E-10	4.77482E-05
3-005-s	2.5416	3.22	4.5	*	0.000571	-2.99632E-10	2.42851E-05
4-005-s	2.5232	3.53	4.69	*	0.000275	-4.55894E-10	1.17699E-05
5-005-s	2.5592	3.84	4.9	*	0.000132	-7.25145E-10	5.57418E-06
6-005-s	2.5041	4.43	5.49		3.39E-05	-2.82114E-09	1.46443E-06
7-005-s	2.5198	5.59	5.77		8.72E-07	-1.99799E-09	3.75041E-08
8-005-s	2.5334	9.28	6.25		-5.6E-07	1.90368E-05	-8.36335E-07
9-005-s	2.5202	10.16	7.15		-7.1E-08	0.000144403	-6.19743E-06
10-005-s	2.5487	10.59	7.48		-3.3E-08	0.000388743	-1.64907E-05
11-005-s	2.5201	10.94	8.49	*	-3.2E-09	0.000867873	-3.72305E-05
12-005-s	2.5531	11.25	9.21	*	-6.1E-10	0.001762061	-7.46125E-05
13-005-s	2.5452	11.49	9.95	*	-1.1E-10	0.00300117	-0.000127476
1-01-s	2.5655	2.78	3.68	*	0.001451	-4.18374E-11	6.11295E-05
2-01-s	2.5551	3.01	4.41	*	0.000938	-2.46807E-10	3.97015E-05
3-01-s	2.551	3.27	4.48	*	0.000504	-2.83374E-10	2.13554E-05
4-01-s	2.5579	3.61	4.79	*	0.000229	-5.75857E-10	9.68926E-06
5-01-s	2.523	3.86	4.91		0.000126	-7.40387E-10	5.38769E-06
6-01-s	2.5114	4.47	5.55		3.11E-05	-3.25301E-09	1.33744E-06
7-01-s	2.5561	5.75	5.93		6.03E-07	-2.88797E-09	2.56417E-08
8-01-s	2.5421	9.95	6.51		-3.1E-07	8.90927E-05	-3.80199E-06
9-01-s	2.6239	10.26	6.91		-1.2E-07	0.000181889	-7.49912E-06
10-01-s	2.5394	10.6	7.59		-2.6E-08	0.000397718	-1.69329E-05
11-01-s	2.5288	10.96	8.71	*	-1.9E-09	0.000906882	-3.877E-05
12-01-s	2.543	11.26	9.28	*	-5.2E-10	0.001800646	-7.65492E-05
13-01-s	2.5205	11.5	9.93	*	-1.1E-10	0.003077164	-0.000131984
1-05-s	2.5127	2.73	4.01		0.001764	-9.6959E-11	7.59112E-05
2-05-s	2.5573	2.96	4.4		0.001057	-2.42069E-10	4.46699E-05
3-05-s	2.5151	3.24	4.63		0.000552	-4.09202E-10	2.37269E-05
4-05-s	2.502	3.55	4.83		0.000267	-6.40602E-10	1.15388E-05
5-05-s	2.511	3.87	5.08		0.000127	-1.12813E-09	5.44974E-06
6-05-s	2.5063	4.54	5.63		2.65E-05	-3.91906E-09	1.14307E-06
7-05-s	2.5643	6.01	5.87		-3.7E-07	2.81983E-09	-1.57904E-08
8-05-s	2.512	9.32	6.2		-6.3E-07	2.08771E-05	-9.25615E-07
9-05-s	2.5136	10.14	6.84		-1.4E-07	0.000137969	-5.94017E-06
10-05-s	2.5244	10.5	7.57		-2.7E-08	0.000315856	-1.35278E-05
11-05-s	2.5132	10.88	8.07		-8.5E-09	0.000757403	-3.25809E-05
12-05-s	2.519	11.16	8.55	*light	-2.8E-09	0.001441892	-6.18819E-05
13-05-s	2.5205	11.44	11.06	*light	-5.1E-12	0.001606075	-6.8887E-05

*= The solution was cloudy even after centrifugation and sitting still for three weeks.

Table A 2. Point-of-Zero-Salt Effect of Clayey Sediment (Lysimeter Sediment).

	Point of Zero Charge pH Testing --Blank				**Point of Zero Charge pH Testing - _Lycimeter**		
	Concentration				**Concentration**		
Tube	**.005M**	**.01M**	**.05M**	**Tube**	**.005M**	**.01M**	**.05M**
1	2.73	2.78	2.8	1	3.36	3.44	3.42
2	2.98	2.96	2.98	2	3.98	3.67	3.91
3	3.25	3.25	3.17	3	4.6	4.57	4.73
4	3.59	3.62	3.78	4	5.03	5.16	5.21
5	3.68	3.85	3.71	5	5.05	5.32	5.08
6	4	4.02	4.13	6	5.37	5.72	5.36
7	5.04	5.56	5.71	7	5.58	5.86	5.69
8	7.27	9.66	8.49	8	6.06	6.27	6
9	8.26	10.08	10.27	9	6.08	6.33	6.45
10	10.69	10.6	10.19	10	6.5	6.73	6.42
11	11.1	11.19	11.04	11	6.99	7.39	7.03
12	11.53	11.55	11.52	12	9.55	9.56	9.1
13	11.84	11.8	11.6	13	10.88	10.83	10.51

Labbook ID:
ESE209, p3

	DH			**DOH**			**DH-DOH**		
Tube	**0.005M**	**0.01M**	**0.05M**	**0.005M**	**0.01M**	**0.05M**	**0.005M**	**0.01M**	**0.05M**
1	0.001425571	0.001296509	0.001204704	-1.75384E-11	-2.15167E-11	-1.99931E-11	0.001425571	0.001296509	0.001204704
2	0.000942416	0.000882682	0.000924102	-8.59493E-11	-3.76534E-11	-7.17331E-11	0.000942416	0.000882682	0.000924102
3	0.000537222	0.000535426	0.000657462	-3.80324E-10	-3.53752E-10	-5.22241E-10	0.000537223	0.000535426	0.000657463
4	0.000247707	0.000232965	0.000159793	-1.03261E-09	-1.40375E-09	-1.56155E-09	0.000247708	0.000232966	0.000159794
5	0.000200017	0.000136467	0.000186667	-1.07416E-09	-2.0185E-09	-1.15098E-09	0.000200018	0.000136469	0.000186668
6	9.57342E-05	9.35938E-05	6.97659E-05	-2.24423E-09	-5.14336E-09	-2.15597E-09	9.57364E-05	9.35989E-05	6.9768E-05
7	6.48984E-06	1.37384E-06	-9.18933E-08	-2.70542E-09	-3.61358E-09	2.30826E-10	6.49255E-06	1.37746E-06	-9.2124E-08
8	-8.1726E-07	-5.36813E-07	-9.96764E-07	1.74727E-07	4.56902E-05	3.0803E-06	-9.9198E-07	-4.6227E-05	-4.0776E-06
9	-8.2626E-07	-4.67652E-07	-3.5476E-07	1.80768E-06	0.000120205	0.000186181	-2.6339E-06	-0.000120673	-0.00018653
10	-3.1620E-07	-1.86184E-07	-3.80125E-07	0.000489747	0.000398053	0.000154855	-0.00049006	-0.00039824	-0.00015523
11	-1.023E-07	-4.07316E-08	-9.33163E-08	0.001258828	0.001548571	0.001096371	-0.00125893	-0.001548612	-0.00109646
12	-2.7888E-10	-2.72604E-10	-7.91308E-10	0.00335296	0.003511826	0.003298722	-0.00335296	-0.003511826	-0.00329872
13	-1.1737E-11	-1.32062E-11	-2.83911E-11	0.006159732	0.00563349	0.003657478	-0.00615973	-0.00563349	-0.00365747

	Soil Weights (g)				DH-DOH		
Tube	**0.005M**	**0.01M**	**0.05M**	**Tube**	**0.005M**	**0.01M**	**0.05M**
1	0.525	0.542	0.523	1	0.000293554	0.000268773	0.000285
2	0.509	0.521	0.513	2	0.000200163	0.00019036	0.000223
3	0.503	0.516	0.52	3	0.000115464	0.00011659	0.000157
4	0.519	0.519	0.52	4	5.15978E-05	5.04354E-05	3.81E-05
5	0.506	0.513	0.509	5	4.27344E-05	2.98902E-05	4.54E-05
6	0.529	0.527	0.505	6	1.9565E-05	1.99559E-05	1.71E-05
7	0.52	0.52	0.51	7	1.3498E-06	2.97636E-07	-2.24E-08
8	0.521	0.514	0.506	8	-2.05839E-07	-1.01051E-05	-9.98E-07
9	0.524	0.511	0.515	9	-5.43418E-07	-2.65337E-05	-4.49E-05
10	0.52	0.493	0.512	10	-0.000101884	-9.07627E-05	-3.76E-05
11	0.517	0.51	0.508	11	-0.000263251	-0.000341179	-0.000267
12	0.506	0.512	0.51	12	-0.000716368	-0.000770678	-0.000801
13	0.518	0.509	0.513	13	-0.001285554	-0.001243569	-0.000883

Table A 3. ICP-MS results from solutions at the end of the equilibration period.

Lab ID	Lab Description	Target pH	Target FA (ppmC)	K(ppb)	Ni(ppb)	Sr(ppb)	Zr(ppb)	Rh(ppb)	Cs(ppb)	Ce(ppb)	Eu(ppb)	Th(ppb)	Final pH
901	3-0-1-Clay	4	0	5635	528.2	533.7	15.7	0.463	205.5	136.0	118.0	29.8	3.76
902	3-0-2-Clay		0	2934	485.2	507.2	8.9	0.457	180.4	107.9	95.9	17.1	3.94
903	3-10-1- Clay		10	5037	511.8	527.7	7.0	0.457	194.4	142.3	125.0	12.0	3.66
904	3-10-2- Clay		10	2264	521.6	537.7	6.4	0.459	177.4	133.6	119.9	10.5	3.80
905	3-30-1- Clay		30	3115	538.4	536.5	6.5	0.459	175.5	117.6	105.6	9.7	3.83
906	3-30-2 Clay		30	3007	537.5	538.1	6.5	0.461	189.5	133.5	119.0	9.3	3.77
907	3-100-1- Clay		100	2917	515.8	534.9	7.6	0.457	168.9	109.7	95.2	9.0	3.79
908	3-100-2- Clay		100	2720	518.2	542.6	8.1	0.464	197.0	121.9	105.0	8.6	3.81
909	3-300-1- Clay		300	7175	386.3	427.4	19.9	0.457	98.9	64.3	66.3	9.5	3.76
910	3-300-2- Clay		300	4489	465.7	502.0	22.5	0.464	175.5	95.4	92.8	9.2	3.68
911	10-0-1- Clay	6.1	0	4749	159.9	190.6	9.4	0.000	85.5	0.5	0.5	19.4	5.10
912	10-0-2- Clay		0	2979	164.3	190.7	6.3	0.000	79.5	1.1	0.9	10.2	5.12
913	10-10-1- Clay		10	1941	69.5	77.0	4.1	0.000	46.6	0.2	0.2	7.3	5.48
914	10-10-2- Clay		10	1781	113.4	136.0	3.6	0.000	62.4	0.2	0.2	6.1	5.29
915	10-30-1- Clay		30	2572	73.0	89.9	3.3	0.000	53.7	0.2	0.2	5.2	5.44
916	10-30-2- Clay		30	2437	122.8	131.4	3.8	0.000	60.8	0.3	0.2	4.8	5.23
917	10-100-1- Clay		100	3933	95.4	107.4	4.3	0.000	62.5	0.9	0.5	4.5	5.32
918	10-100-2- Clay		100	2399	167.6	187.5	4.8	0.000	79.6	1.5	2.0	4.5	5.00
919	10-300-1- Clay		300	3060	62.3	63.9	37.8	0.000	44.0	22.9	29.1	6.2	5.57
920	10-300-2- Clay		300	2707	57.8	54.8	27.4	0.000	2.1	11.2	17.5	5.5	5.20
921	11-0-1-CLAY	8.7	0	6167	0.8	40.8	55.9	0.012	47.8	0.4	0.5	21.7	8.25
922	11-0-2-CLAY		0	3176	22.1	60.3	3.9	0.012	46.6	0.2	0.3	5.9	6.21
923	11-10-1-CLAY		10	3474	7.7	55.3	4.7	0.007	46.8	0.2	0.3	5.4	6.62
924	11-10-2-CLAY		10	3263	31.9	85.3	2.5	0.008	56.8	0.2	0.2	4.3	5.72
925	11-30-1-CLAY		30	2251	6.8	51.7	4.7	0.007	43.8	0.2	0.3	4.4	6.73
926	11-30-2-CLAY		30	1366	7.5	40.5	4.0	0.005	24.9	0.2	0.3	3.8	6.59
927	11-100-1-CLAY		100	2303	28.6	70.6	3.8	0.006	45.7	0.6	1.2	3.6	5.81
928	11-100-2-CLAY		100	2876	19.0	56.9	3.7	0.005	44.9	0.8	1.3	3.4	6.15
929	11-300-1-CLAY		300	3191	55.9	48.4	54.7	0.006	21.3	52.8	42.0	12.8	7.15
930	11-300-2-CLAY		300	1560	48.8	40.7	63.4	0.005	20.8	44.6	41.3	12.0	6.27

931	4-0-1-SAND	4.1	0	2847	567.7	530.4	49.2	0.000	324.4	101.2	108.7	21.5	3.80
932	4-0-2-SAND		0	1103	550.0	511.6	17.0	0.000	328.2	85.2	91.4	6.7	4.01
933	4-10-1-SAND		10	1626	535.9	509.2	12.8	0.000	319.5	78.9	83.8	4.4	4.04
934	4-10-2-SAND		10	1331	520.9	506.7	10.4	0.000	320.8	63.9	68.5	3.1	4.17
935	4-30-1-SAND		30	1168	516.4	516.4	9.6	0.000	329.8	65.0	70.9	2.5	3.89
936	4-30-2-SAND		30	1056	497.0	482.1	8.7	0.000	307.6	37.6	42.8	2.3	4.15
937	4-100-1-SAND		100	1071	463.2	415.9	78.1	0.000	270.5	51.2	79.7	6.0	4.04
938	4-100-2-SAND		100	1753	469.8	435.7	84.1	0.000	292.5	57.7	85.9	6.8	3.99
939	4-300-1-SAND		300	1368	382.8	365.5	472.7	0.000	198.6	163.3	218.6	31.6	3.98
940	4-300-2-SAND		300	1421	392.8	410.6	642.9	0.000	216.9	191.7	222.3	44.6	3.99
941	8-0-1-SAND	5.5	0	4849	390.1	343.3	19.9	0.106	288.3	11.3	16.0	18.2	5.49
942	8-0-2-SAND		0	1217	344.2	305.5	12.0	0.102	228.2	2.8	2.9	5.7	5.41
943	8-10-1-SAND		10	912.3	328.0	286.3	5.2	0.099	220.5	0.8	1.1	3.6	5.40
944	8-10-2-SAND		10	960.5	374.5	336.6	2.0	0.100	257.4	5.7	6.3	2.7	5.33
945	8-30-1-SAND		30	1196	294.6	267.3	3.3	0.101	213.0	5.0	9.4	2.3	5.31
946	8-30-2-SAND		30	874.9	266.1	236.3	2.0	0.099	204.4	4.2	8.4	1.8	5.37
947	8-100-1-SAND		100	1391	438.9	424.5	203.5	0.108	318.5	87.1	101.0	9.2	5.23
948	8-100-2-SAND		100	1391	248.4	199.9	151.3	0.096	136.6	59.0	90.1	12.9	5.17
949	8-300-1-SAND		300	1356	268.7	152.7	584.2	0.097	82.7	204.3	239.2	38.7	5.24
950	8-300-2-SAND		300	1372	319.6	197.4	665.7	0.096	154.0	236.0	272.8	44.1	5.22
951	9-0-1-SAND	7.2	0	2968	45.8	93.0	135.4	0.000	183.6	0.8	13.7	13.3	6.56
952	9-0-2-SAND		0	1615	37.0	89.3	25.1	0.000	168.7	0.2	0.1	4.6	6.70
953	9-10-1-SAND		10	1594	23.3	76.2	19.3	0.000	156.0	0.2	0.3	3.2	6.83
954	9-10-2-SAND		10	1714	23.6	76.3	14.3	0.000	164.2	0.2	0.3	2.5	6.85
955	9-30-1-SAND		30	1494	45.0	80.4	14.6	0.000	173.2	7.6	10.2	2.6	6.59
956	9-30-2-SAND		30	2302	31.1	77.3	18.7	0.000	167.7	10.4	12.3	3.1	6.83
957	9-100-1-SAND		100	1524	148.5	94.6	156.8	0.000	142.2	111.2	124.4	23.5	6.52
958	9-100-2-SAND		100	1725	161.4	108.7	177.4	0.000	146.3	123.1	135.8	27.6	6.61
959	9-300-1-SAND		300	1499	331.2	164.2	481.4	0.000	145.2	277.1	291.5	48.2	6.59
960	9-300-2-SAND		300	1788	334.3	170.8	539.1	0.000	140.0	274.6	291.7	52.0	6.55
NO-SEDIMENT CONTROLS													
961	4-0-1-NOSOLID	4.1	0	10630	567.9	450.0	1502.0	0.000	533.7	534.3	550.3	168.7	4.06
962	4-0-1-NOSOLID		0	4293	542.7	455.7	932.2	0.000	523.1	439.8	526.0	124.9	4.29
963	4-10-1-NOSOLID		10	6588	550.4	459.7	1270.0	0.000	503.2	481.5	489.3	132.2	4.20
964	4-10-1-NOSOLID		10	3097	566.7	464.3	1311.0	0.000	507.2	422.4	434.0	111.2	4.00
965	4-30-1-NOSOLID		30	2810	628.8	498.6	1465.0	0.000	519.6	504.9	513.4	138.0	3.95

966	4-30-1-NOSOLID		30	2960	608.1	482.5	1521.0	0.000	506.8	494.4	502.6	140.0	3.96
967	4-100-1-NOSOLID		100	22260	603.7	482.6	1431.0	0.000	512.2	517.2	520.8	132.6	4.13
968	4-100-1-NOSOLID		100	3514	596.0	473.0	1608.0	0.000	518.4	534.5	538.1	151.3	4.08
969	4-300-1-NOSOLID		300	3730	594.5	480.3	1199.0	0.000	504.9	545.8	542.3	109.1	4.00
970	4-300-1-NOSOLID		300	4115	634.0	482.7	1135.0	0.000	511.2	541.7	536.9	106.5	3.99
971	8-0-1-NOSOLID	8	0	2809	423.2	416.2	671.1	0.239	424.8	0.6	39.0	15.1	7.67
972	8-0-2-NOSOLID		0	1400	471.0	431.7	623.2	0.248	428.8	0.4	0.4	4.3	7.58
973	8-10-1-NOSOLID		10	1450	497.3	422.4	1396.0	0.241	479.2	463.4	447.2	130.0	7.39
974	8-10-1-NOSOLID		10	2230	483.8	428.0	1515.0	0.246	483.8	504.3	486.2	144.1	7.45
975	8-30-1-NOSOLID		30	2113	459.2	404.3	1536.0	0.242	470.1	504.0	502.8	129.5	7.39
976	8-30-1-NOSOLID		30	1473	488.5	421.2	1725.0	0.242	497.2	499.4	503.7	131.2	7.16
977	8-100-1-NOSOLID		100	1879	508.6	440.6	1265.0	0.247	473.7	535.0	532.0	109.6	7.39
978	8-100-1-NOSOLID		100	1833	590.2	470.8	1584.0	0.245	513.9	578.2	576.9	113.1	7.26
979	8-300-1-NOSOLID		300	1989	522.8	447.2	808.4	0.245	454.1	510.8	496.9	48.8	7.20
980	8-300-1-NOSOLID		300	1620	503.4	434.7	749.1	0.246	428.1	484.5	475.0	49.9	7.25

Table A 4. Titration curve data for the sandy and red-clay sediments.

Clay pH	meq added to Clay (meq/g)**	Sand pH	meq added to Sand (meq/g)**
3.125	-0.02499	2.785	-0.02499
3.495	-0.014988	3.025	-0.0149895
4.17	-0.0040004	3.75	-0.003998
4.36	-0.0019994	4.11	-0.0019996
4.485	-0.0005	4.535	-0.0005
4.53	0	4.72	0
4.59	0.0005	4.955	0.0005
4.75	0.0020004	5.52	0.0019988
4.935	0.0039992	7.305	0.0039996
6.07	0.014997	10.54	0.0149925
8.73	0.0249775	10.91	0.024995

** Negative values are for acid additions, positive values are for base additions.
Average of 2 replicates.