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INFLUENCE OF DISSOLVED ORGANIC CARBON AND pH ON IODIDE, PERRHENATE, AND SELENATE SORPTION TO SEDIMENT

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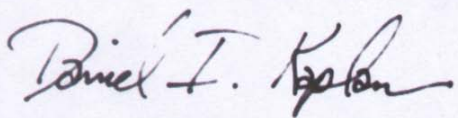
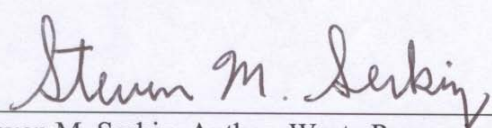
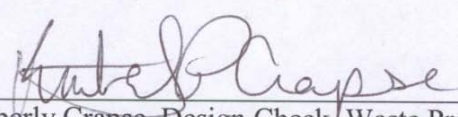
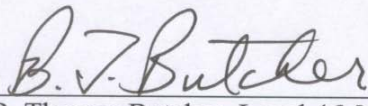
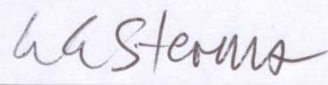

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ACRONYMS

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
OC	Organic Carbon
PA	Performance Assessment
SRS	Savannah River Site
NOM	Suwannee River Natural Organic Matter
XRD	X-ray Diffraction

1.0 ABSTRACT

Low-Level Waste buried on the Savannah River Site contains cellulosic materials, including wood, paper, and cardboard. Once buried, these cellulosic materials are expected to degrade to form cellulose degradation products (CDP), which in turn are expected to influence radionuclide speciation. Under certain pH ranges and CDP concentrations, it is expected that radionuclides will sorb less to the subsurface sediments due to the formation of poorly sorbing complexes and/or competition for surface sorption sites by the anionic in nature CDPs and therefore migrate more rapidly from the disposal site, than in the absence of CDP. Previous CDP-impacted K_d values were based on laboratory work and generalized surface complexation modeling with cations (Kaplan and Serkiz 2005; Serkiz and Kaplan 2006). The objective of this study was to quantify the influence of CDP and pH on anion sorption to two SRS subsurface sediments: a subsurface clayey and subsurface sandy sediment. The intent was to provide values for direct use for future performance assessment calculations.

Perrhenate (ReO_4^- , as an analogue for pertechnetate, TcO_4^-), selenate (SeO_4^{2-}), and iodide (I^-) were used as anions of interest. Fulvic acid, a naturally occurring organic material, was used as an analogue for CDP. ReO_4^- and I^- essentially did not sorb to the sediment, irrespective of CDP or pH values. Conversely, selenate sorbed very strongly to the sediment; the K_d value was >1040 mL/g for the sand and clay sediments at most pH and fulvic acid concentrations. In the sandy sediment, but generally not in the clayey sediment, as the fulvic acid concentrations increased, the selenate K_d values decreased. The resulting recommended CDP- K_d values for I and Tc (based on Re) will not differ from non-CDP-impacted K_d values. These are the first SeO_4^{2-} sorption tests using SRS sediments; therefore they provide site specific values for both CDP and regular conditions. Original “Soil K_d ” values were 5 mL/g, reflecting a great deal of uncertainty due to lack of site-specific measurements (McDowell-Boyer *et al.* 2000). Thus, these values provided evidence that a great deal more radio-selenium sorption occurs than previously believed.

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) 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.

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 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 U(VI), UO_2^{2+} , and Eu(III), Eu^{3+} , 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 natural organic matter (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 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 (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 present or absent.

In previous modeling for the performance assessment (McDowell-Boyer *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.

Kaplan and Serkiz (2004) measured sorption as a function of fulvic acid (CDP analogue) and pH for several solutes, including monovalent cations (K^+ and Cs^+), divalent cations (Ni^{2+} and Sr^{2+}), trivalent cations (Ce^{3+} and Eu^{3+}), and tetravalent cations (Th^{4+} and Zr^{4+}). Analogues were matched to ~30 radionuclides based on similarities in periodicity and chemical properties. They created a look-up K_d table that listed the 30 radionuclides as a function of pH and CDP (total carbon concentration). This data was further refined through complexation modeling in Serkiz and Kaplan (2006). These values have since been used as the bases for the CDP-corrected K_d values recommended for use in the performance assessment (Kaplan 2006).

3.0 OBJECTIVE

The objective of this study was to measure sorption of perrhenate (ReO_4^- , as an analogue for pertechnetate, TcO_4^-), selenate (SeO_4^{2-}), and iodide (I^-) to E-Area sediments and to determine the impact of fulvic acid and pH on the sorption process.

4.0 MATERIALS AND METHODS

Details of the materials and methods are presented in Section 9.0: Appendix A. A brief description of the experiment's materials and methods are described here. The experimental design was an incomplete factorial including two replicates, two sediments (sandy sediment and a clayey sediment from the E-Area subsurface environment), three pH levels (approximately 3.9, 5.3 and 6.7), five DOC levels (0 to 300 mg/L C from Suwannee River – Natural Organic Matter (NOM) reverse osmosis isolate; International Humic Substances Society, St. Paul, MN), and three elements (Re, Se and I; from a ICP-MS stock solution; Fisher Scientific, Pittsburgh, PA). Batch contact experiments were conducted in 50-mL centrifuge tubes with 5-g sediment and 50-mL liquid. The anions were added as ReO_4^- , SeO_4^{2-} , and I^- .

Complexity was added step-by-step to the system under study; first only an aqueous system was studied, then sediment, DOC, then finally the anions. Between each addition, the pH was adjusted if necessary and appropriate measurements were taken. Briefly, 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. This information was used to create a point of zero-point-of-salt-effect, a measure of the pH level where the sediment surface has a net zero charge. Then varying concentrations of DOC were added to the pH adjusted tubes; after a one-week equilibration period, pH levels were measured. Again, acid or base was added if necessary to maintain the system at the targeted pH. 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 controls were included in this study, approximately 1 control for every 3 samples. No-sediment controls were included to permit calculating the zero-point-of-salt-effect. No-NOM controls were included to provide a measure of how well the I, Re, and Se sorbed in the absence of NOM. No-solute controls were included to provide a measure of how well the NOM sorbed to the sediment in the absence of the anions. Finally, there were anion-NOM (no sediment) studies conducted to determine how well the anions complex with the NOM in the absence of a sediment surface present competing for the anion.

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 five 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% HNO₃. The pH and DOC samples were not preserved prior to analysis.

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 mineralogical 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 1). 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). As mentioned earlier, 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 these minerals were present at concentrations $\geq 5\%$. 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 as great a pH changes in response to varying CDP concentrations leaching from the low-level waste.

Table 1. 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.

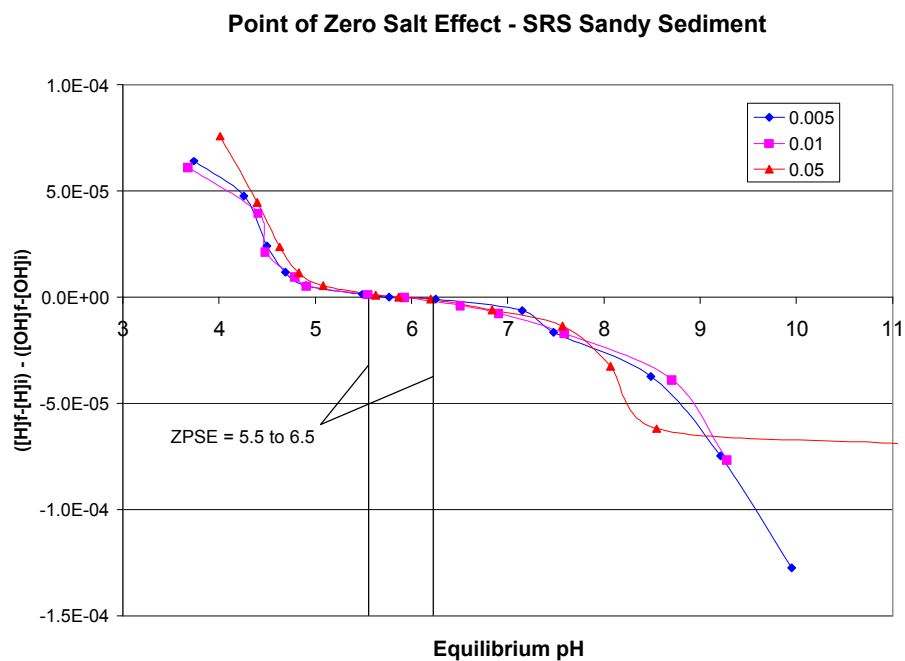


Figure 1. Point-of-Zero-Salt Effect (approximately the pH at which sediment has a net charge of zero) of the sandy sediment conducted at three ionic strengths (the PZSE is at pH 5.5 to 6.5).

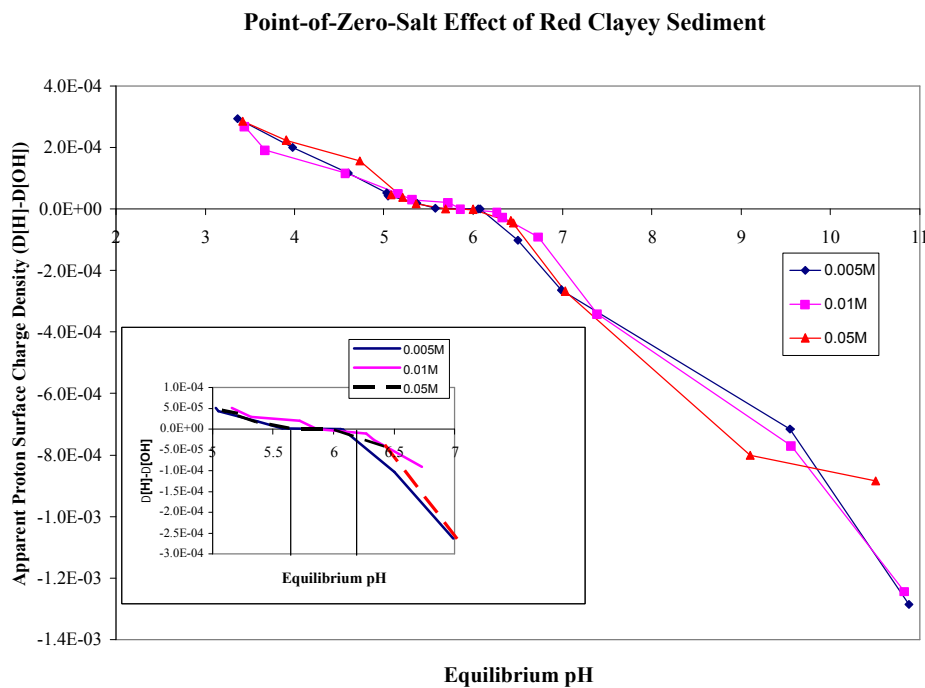


Figure 2. Point-of-Zero-Salt Effect for the Red Clay Sediment conducted at three ionic strengths (PZSE = pH 5.6 to 6.2).

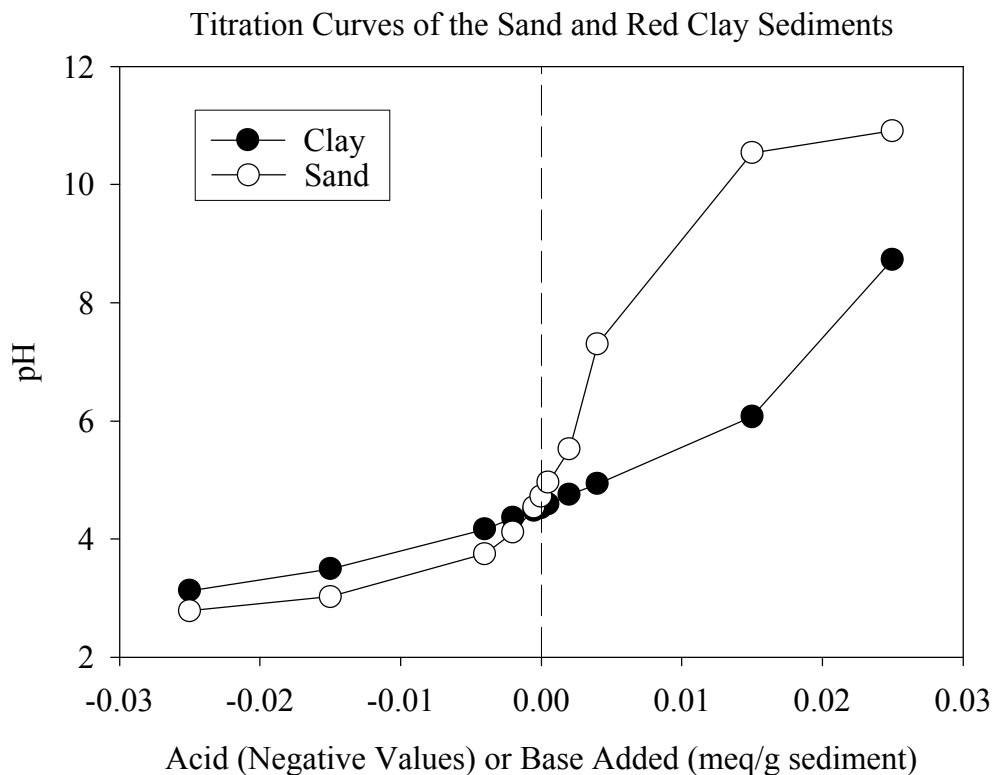


Figure 3. Titration of the sand and clay sediments.

5.2 Organic Matter Interactions with the Sediments

After the sediment suspensions were pH adjusted, varying amounts of NOM were added. The DOC concentrations in the no-sediment controls are presented in Table 2. 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 powdered 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 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 2. 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 2 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 3 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 (Table 1). 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 the anionic nature of various NOM functional groups.

Table 3. Dissolved and sorbed organic carbon concentrations at end of experiment.

pH	Targeted DOC Addition (mg/L C)	Actual DOC Addition (mg/L C)	Clayey Sediment		Sandy Sediment	
			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.

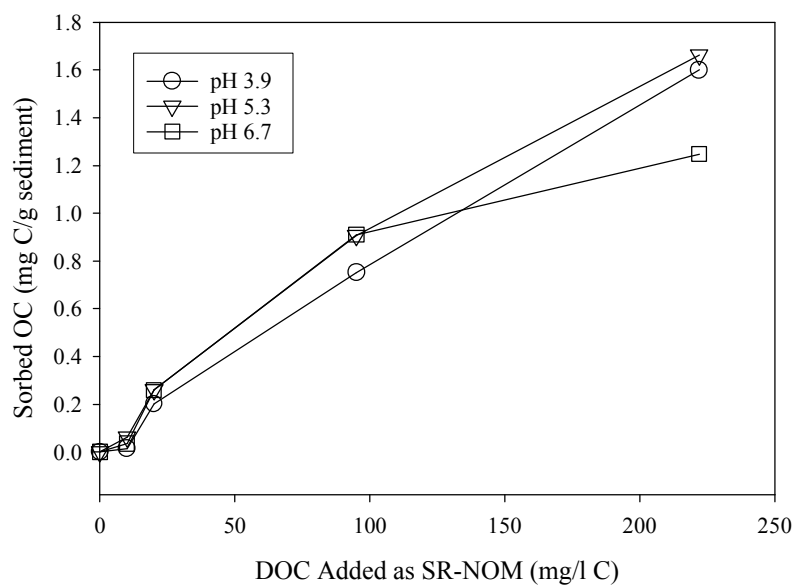
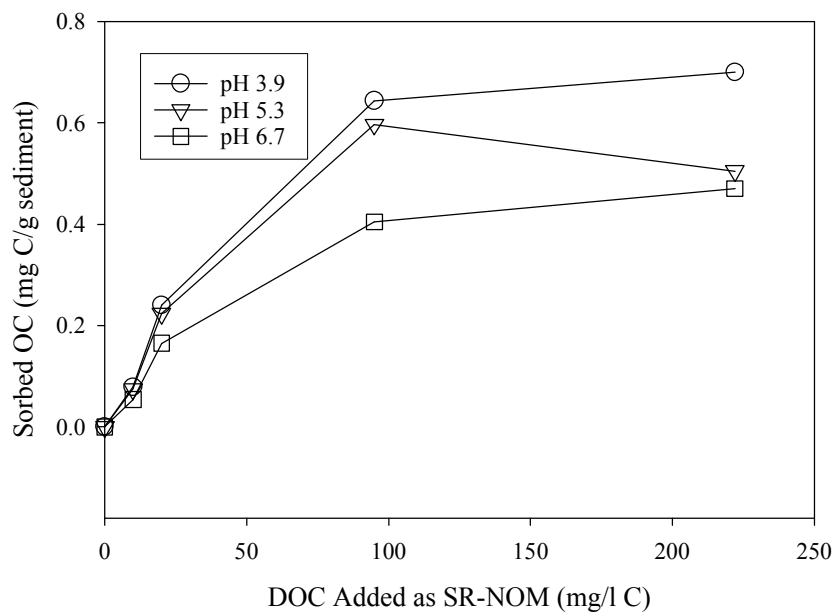
Sorbed OC vs. Added DOC: Clayey Sediment**Sorbed OC vs. Added DOC: Sandy Sediment**

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 NOM Controls

A number of controls were included in this study, approximately 1 control for every 3 samples. The no-sediment 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. We elected to evaluate only the extreme pH levels because we did not anticipate any effect. The final pH values of these controls as a function of NOM concentrations are reported in Figure 5. This shows that the pH values remained essentially constant as a function of targeted NOM concentration. The importance of this is that the natural tendencies of pH values is to decrease as NOM concentrations increase were overcome by acid and base additions. Thus, NOM and pH were in fact independent variables in this set of controls, consistent with the experimental design and ruling out a potential and common experimental artifact.

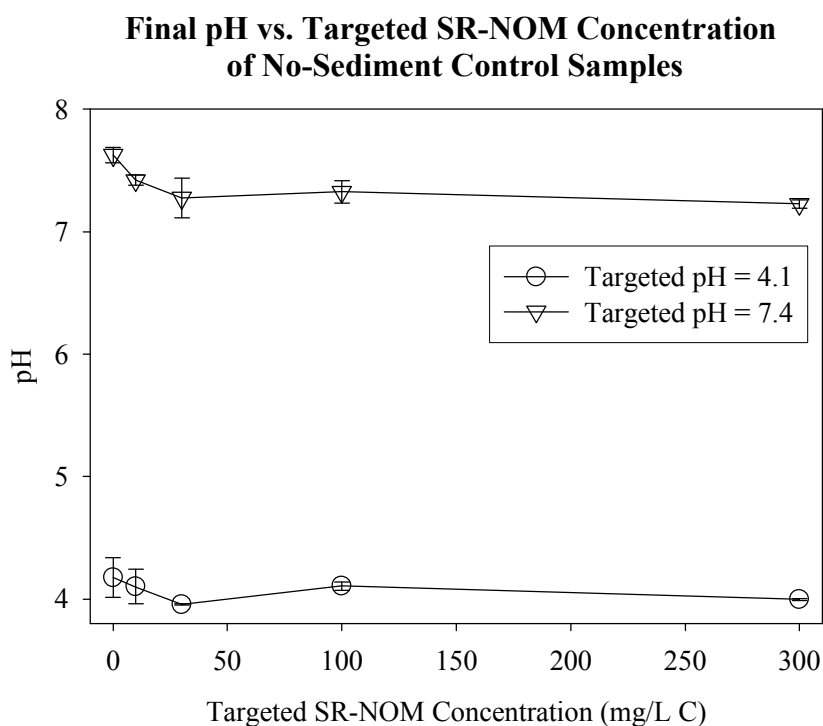


Figure 5. Final pH vs. targeted natural organic matter concentration of no-sediment control samples (2 observations for each mean and standard deviation).

5.3.2 Contaminant Spike Controls

Another concern regarding the contaminant amendments was to determine how soluble they remained as a function of pH and NOM and whether sorption occurred to glassware, both experimental artifacts. Re, Se, and I aqueous concentrations at pH 5.3 remained fairly constant as a function of NOM concentrations. Only one pH was selected as a control between the two extremes, pH values 4 and 7. Considering the means and standard deviation bars, there was not a systematic change in solute concentrations as a function of NOM concentrations (Figure 6).

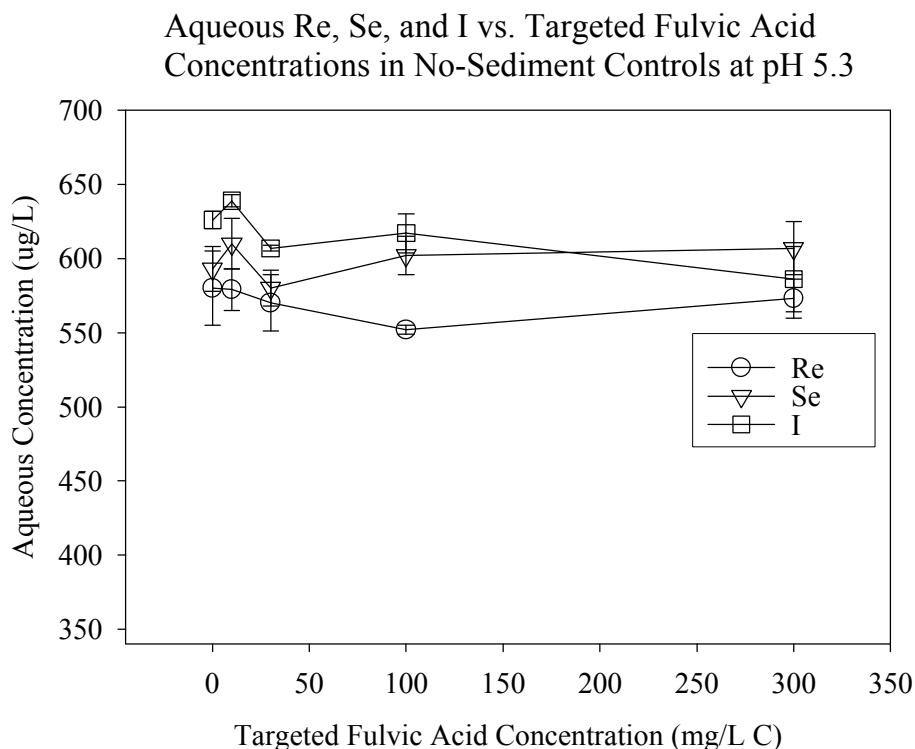


Figure 6. Aqueous Re, Se and I versus targeted NOM concentrations in the no-sediment controls at pH 5.3.

5.3.3 I, Re, and Se Sediment Sorption

Perrhenate, ReO_4^- , was used in these experiments as an analogue for pertechnetate, TcO_4^- . The other two species used in these experiments were selenate, SeO_4^{2-} , and iodide, I^- . ReO_4^- and I^- sorbed very weakly to the sediment, resulting in K_d values that did not differ significantly from 0 mL/g, irrespective of NOM or pH values (Table 4 and Table 5). Especially in the case of the iodine, there were negative K_d values; these were likely the result of analytical error, since

negative sorption in this case makes little physical sense.¹ It is important not to over interpret the ReO_4^- and I^- , that is to look through the data for trends, because the error terms suggest that many of the means do not differ significantly from 0 mL/g.

Conversely, selenate sorbed very strongly to the two sediments; the K_d values were >1000 mL/g for the sandy and clayey sediments for most pH values and NOM concentrations (Table 6 and Figure 7). Due to the lower sorption capacity in the sandy sediment, the selenate K_d values decreased as the NOM concentrations increased (the NOM occupied sorption sites or the NOM complex the selenate, keeping the Se in the aqueous phase and reducing its tendency to sorb to the sediment).

On the clayey sediment, there was no sorption response at pH 3.9; the K_d values remained constant at ~ 1041 mL/g. As the pH was increased to 5.3 and 6.7, more Se sediment sorption occurred as the NOM concentration increased up to 100 mg/L C. Presumably, at <100 mg/L C the added NOM sorbed to the sediment providing more sorption sites for the Se to partition to. At the highest NOM loading, the sediment binding sites were totally filled and the excess NOM remained as DOC, which complexed the Se, not permitting it to bind to the sediment. Similar trends were observed with the sandy sediment except that because the sandy sediment contained fewer sorption sites than the clayey sediment, the decrease in K_d values due to the increase in NOM was observed at lower NOM concentrations.

It is well known that selenite, SeO_3^{2-} , the reduced form of selenate, sorbs more strongly than selenate to sediments at all pH levels (Balistrieri and Chao 1990; Elrashidi *et al.* 1987; Balistrieri and Chao 1987). On oxide surfaces, selenite adsorbs by ligand exchange, a process resulting in direct contact between the selenite and oxide surfaces. X-ray absorption studies have shown that selenate forms outer-sphere complexes with oxide surfaces, bonds where water molecules exist between the Se and the oxide surface, whereas selenite ions form strong direct bonds to the oxides surfaces without the water molecules present (Hayes *et al.* 1987). The extremely high sorption values measured in this study may be attributed to: 1) simply high selenate sorption, 2) selenate reduction to selenite followed by inner-sphere complexation to surface sites, 3) Se precipitation, and 4) co-precipitation with Fe(III), analogous to what is commonly found in nature with As. If selenate is being reduced in the study system, it does not appear to be induced by the fulvic acid because the high K_d values were observed in the 0 mg/L NOM treatments. It is possible that reduction may have been caused by the sediment itself, *i.e.*, via surface induced chemical reduction. Using precisely this clayey sediment, we observed that Pu(V) was reduced to Pu(IV) (Kaplan *et al.* 2005). Elrashidi *et al.* (1987), reports that selenite would be maintained at 10^{-8} M Se in conditions expected for SRS sediments, the Se concentration measured in the clayey sediments ($5 \mu\text{g/L} = 6.3 \times 10^{-8}$ M). Finally, it is entirely possible that selenate could be sorb in high concentrations by sediments. Balistrieri and Chao (1990) demonstrate just slightly lower, $\sim 10\%$, selenate than selenite sorption values to Fe- oxyhydroxide. However, the extremely high sorption and the lack of trends with the NOM are not consistent with much of the literature, suggesting that the simplest explanation of high sorption of selenate is less probable. Additional tests are required to determine the sorption mechanism.

¹ Negative K_d have also been used to describe anion exclusion, resulting from anions being repulsed from negatively charged sediment surfaces. Such phenomena are typically measured in column studies by have also mean measured in batched studies (Kaplan and Serne 1995).

Table 4. I K_d values (mL/g; n = 2).

Target 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	-0.2	0.2	0.1	0.4	0.2	0.1	-0.1	0.9	-0.2	0.2	0.1	0.1
10	0.2	0	-0.4	0.2	0.0	0.1	-0.3	0.1	-0.4	0.2	-0.4	0.1
30	-0.3	0.5	-0.2	0.1	-0.5	0.2	-0.7	0.2	-0.7	0.1	-0.6	0.3
100	-0.4	0	-0.6	0.1	-0.5	0.0	-0.3	0.2	-0.6	0.3	0.1	0.2
300	-0.3	0.2	-0.6	0.3	-0.8	0.6	-0.3	0.4	0.0	0.3	0.2	0.0
Avg	-0.2		-0.3		-0.3		-0.3		-0.4		-0.1	
Stdev	0.2		0.3		0.4		0.2		0.3		0.3	

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

Table 5. Re K_d values (mL/g; n = 2).

Target 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	0.6	0.3	0.1	-0.1	0.3	-0.4	0.3	-0.2	0.4	0.0	0.2
10	0.3	0.1	0.2	0.0	0.2	0.0	0.0	0.21	-0.3	0.2	0.0	0.2
30	0.1	0.6	0.2	0.1	0.0	0.3	-0.1	0.2	0.0	0.3	-0.4	0.3
100	0.4	0.1	0.0	0.0	0.3	0.0	0.2	0.2	-0.3	0.3	0.3	0.1
300	0.4	0.0	0.3	0.4	0.8	0.0	0.0	0.7	0.3	0.7	0.2	0.1
Avg	0.1		0.2		0.0		-0.1		-0.1		0.0	
Stdev	0.3		0.1		1.0		0.3		0.4		0.2	

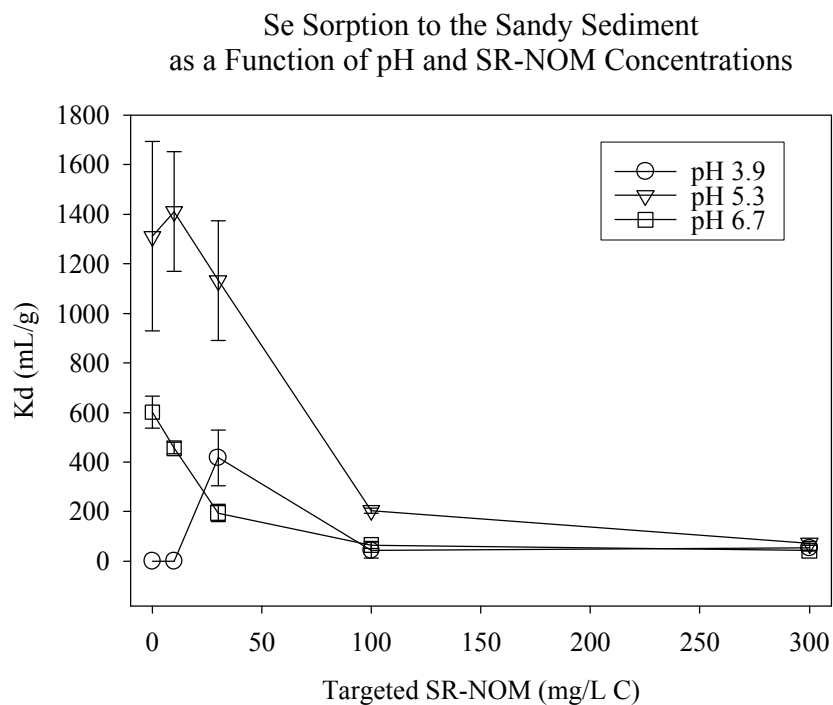
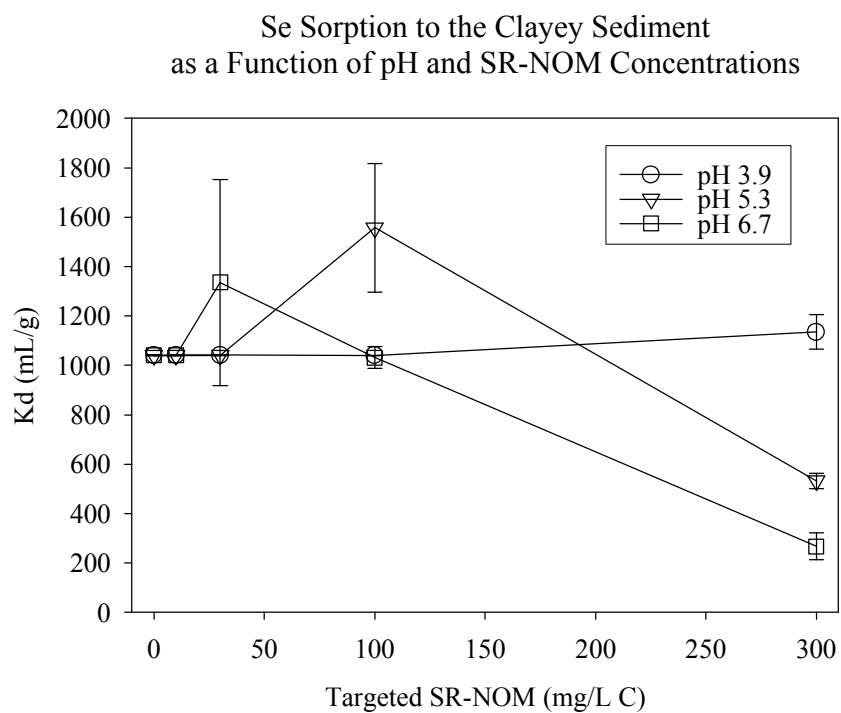


Figure 7. Se K_d values as a function of pH and NOM concentrations in clayey (top) and sandy (bottom) sediments. All K_d values greater than 1000 mL/g are “greater than” values.

Table 6. Se K_d values (mL/g ; n = 2).

Target 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	1041	1	1041	4e-1	1041	3e-1	1041	0	1311	383	601	65
10	1041	0	1041	3e-1	1041	1e-1	1041	0	1411	241	456	23
30	1041	3e-1	1041	3e-1	1336	417	1661	112	1133	241	195	35
100	1041	3e-1	1557	261	1031	44	483	33	204	10	65	16
300	1135	70	533	32	267	54	169	12	72	9	43	1

6.0 RECOMMENDATIONS

The Performance Assessment uses CDP-Correction Factors, $f_{CDP,pH,C}$, to change traditional K_d value to account for the presence of CDP in systems (Kaplan 2005). These correction factors change as a function, not only of radionuclide, but also of soil, pH and CDP concentration. So, as such, they are not especially robust geochemical parameters. The CDP-Correction Factors were calculated using the K_d data in this report (Table 4, Table 5, and Table 6):

$$f_{CDP,pH,C} = \frac{Kd_{CDP,pH,C=x}}{Kd_{pH,C=0}} \quad (1)$$

The numerator, $Kd_{pH,C=x}$, is a measure of the radionuclide Kd value with a sediment at a given pH and organic carbon content dissolved in the solution. The denominator, $Kd_{pH,C=0}$ is a measure of the radionuclide K_d value with the same sediment and the same pH, but without any CDP present in the solution. The CDP-correction factor was used to calculate a CDP-corrected Kd value, Kd_{CDP} :

$$Kd_{CDP} = f_{CDP} \times Kd . \quad (2)$$

The CDP-Correction Factors were calculated for pH 5.3 (background) (Table 7). A conservative assumption that was made in these calculations was:

$$\text{Assumption:} \quad f_{CDP,pH,C} \leq 1.0 \quad (3)$$

CDP-Correction Factors were frequently found to be >1.0 , especially for the clayey sediment and at lower NOM concentrations (Figure 7). This was also found true for metals (Kaplan and Serkiz 2005). By making the assumption described in Equation (3), the K_d will never be enhanced due to the presence of CDP.

7.0 CONCLUSIONS

The resulting recommended CDP- K_d values for I and Tc (based on Re) will not influence regular, non-CDP-impacted, K_d values. These are the first SeO_4^{2-} sorption tests using SRS sediments; therefore they provide site specific values for both CDP and regular conditions. Original “Soil K_d ” values were 5 mL/g, reflecting a great deal of uncertainty due to lack of site-specific measurements (McDowell-Boyer et al. 2000). Thus, these values, which were generally >1000 mL/g, provide evidence that a much greater sorption occurs than previously thought was the case. These larger K_d values may permit greater amounts of radio-selenium to be safely disposed in the E-Area Low-Level Waste facility.

Table 7. CDP Correction Factors assuming no enhanced sorption due to presence of CDP and CDP-Corrected Kd values at pH 5.3.

Radio-nuclide	“Best” Sediment K _d ^(a) (mL/g)	CDP Correction Factors Assuming No Enhanced Sorption in the Presence of DOC				CDP Corrected Kd (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
I – Clay	0.6	1.0 ^(b)	1.0 ^(b)	1.0 ^(b)	1.0 ^(b)	0.6	0.6	0.6	0.6
I – Sand	0	1.0 ^(b)	1.0 ^(b)	1.0 ^(b)	1.0 ^(b)	0	0	0	0
Tc – Clay	0.1	1.0 ^(b)	1.0 ^(b)	1.0 ^(b)	1.0 ^(b)	0.1	0.1	0.1	0.1
Tc – Sand	0.2	1.0 ^(b)	1.0 ^(b)	1.0 ^(b)	1.0 ^(b)	0.2	0.2	0.2	0.2
Se –Clay	1000	1.0	1.0	1.0	0.5	1000	1000	1000	500
Se - Sand	1000	1.0	1.0	0.2	0.07	1000	1000	200	70

^(a) “Best” K_d values from Table 10 in Kaplan (2006), which are presently being used for PA calculations. Equations 1 – 3.

^(b) Essentially no I or Tc sorption to the sandy or clayey sediment was observed. Therefore it was not possible to determine a correction factor (any value divided by zero is undefined). Values of unity are entered in this table with this caveat. The fact that no I or Tc sorption was detected bring up the issue of why non-zero K_d values are entered as “Best Sediment K_ds”. This will have to be addressed in the future.

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9.0 APPENDIX A: DETAILED DESCRIPTION OF MATERIALS AND METHODS

Influence of Natural Organic Matter on I, Se, and Re Sorption to SRS Sediments

Objective: The overall objective of this study is to create input geochemistry values for PA calculations related to I, Re, and Se sorption to E-Area sediment in the presence of cellulose degradation products. The specific objectives are to determine sorption envelopes (sorption vs. pH) of I, Re, and Se as a function of fulvic acid concentrations.

Materials:

1. 100 50-mL centrifuge tubes
2. Grand Canyon Subsurface Sandy sediment
3. subsurface clayey sediment
4. 2.0-L 0.02 M NaCl
5. 0.5-L 1 M HCl
6. 0.5-L 1 M NaOH
7. 0.5-L 0.1 M NaOH
8. 0.5-L 0.1 M HCl
9. 5 100-mg Suwannee River Natural Organic Matter (NOM; reverse osmosis isolation; International Humic Substances Society, Catalog Number 1R101N)
10. 65-mL 10,000 mg/L Fulvic Acid Stock: dissolve 0.65g IHSS Fulvic Acid (FA; Suwannee River Fulvic Acid) in 65mL water. Mix well. Store in refrigerator and in light-proof or amber glass container.
11. 70-mL 1000 mg/L Fulvic Acid Stock: Add 7 mL of 10,000 mg/L FA Stock solution to a beaker. Add 63 mL water. Mix well. Store in refrigerator and in light-proof or amber glass container.
12. ICP-MS standards stock solution
13. 1000 ppm I stock solution:
 - 1 - Add 0.327 g KI to a 250-mL volumetric flask;
 - 2 - dissolve in ~150 mL of 0.001 M NaOH, and
 - 3 - bring up to volume with 0.001 M NaOH.
14. 120 ppm Re, Se, and I stock solution:
 - 1 - Add 12 mL of 1000 ppm Re standard to a 100-mL volumetric flask.
 - 2 - Add 12 mL of 1000 ppm Se standard to 100-mL volumetric flask.
 - 3 - Add ~40 mL water. Using litmas paper, adjust pH to 4 to 7 with 0.1 or 0.01 M NaOH.
 - 4 - Add 12 mL of 1000 ppm I standard to 100-mL volumetric flask.
 - 5 - Bring up to volume with water.

Methods:

1. Label tubes as shown in Table 1 and record tare weights.
2. Add 5.00 g of appropriate sediment to treatment tubes, no sediment to controls (Sample IDs 161 through 170). Record actual sediment weight in Table 1.
3. Add 40-mL of 0.02 M NaCl.
4. Add appropriate amount of NOM to each tube as shown in Table 1.
5. Add 0.25-mL of 120-ppm Re, Se, and I stock solution to each tube. Shake tubes by hand for ~5 seconds.
6. pH adjust solutions by adding either 0.1 M NaOH or 0.1 M HCl. We want to add <2 mL of solutions so it may be better to add 1 M HCl and 1 M NaOH.
7. Put suspension in box and the box in a refrigerator over night.
8. On the following day, pH adjust again. Don't worry about waiting for tubes to come to room temperature
9. Measure weight of each tube and contents. Show me these weights and we'll decide what weight to target for the next step.
10. Record in Table 1 how much water needs to be added to each tube to create equal volumes. Add water to tubes.
11. Record final weight in Table 1.
12. Put suspensions in box and the box in a refrigerator. Shake box vigorously 2 times a day for 1 week.
13. After the 1 week equilibration period, remove suspensions from refrigerator. Measure pH and record in Table 1.
14. Centrifuge tubes, recover aqueous. (Do not acidify samples.)
15. Transfer 10-mL of each sample into a vial (plastic or glass is OK) and then submit vials to UGA for ICP-MS analysis.
16. We will use the remaining volume of each sample for DOC analyses using Anna Knox's DOC analyzer.

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

Waste: Non-rad and non-hazardous waste. Check if Cl is an issue for disposing down sink. 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 page11.

Table 1. Sample ID, description, pH, and weights.

Sample ID	Sediment	pH	NOM (ppm C)	Tare Wt (g)	Tare + Sediment wt. (g)	NOM added (mL/Stock ppm)	Tube wt. after last pH adjustment	Added water to make equal vol. (mL)	Final Vol (mL)	Final pH
Procedure Step				1	2	4	9	10	11	13
101	Clay	3.9	0			0				
102			0			0				
103			10			1-1,000				
104			10			1-1,000				
105			30			3-1,000				
106			30			3-1,000				
107			100			1-10,000				
108			100			1-10,000				
109			300			3-10,000				
110			300			3-10,000				
111		5.3	0			0				
112			0			0				
113			10			1-1,000				
114			10			1-1,000				
115			30			3-1,000				
116			30			3-1,000				
117			100			1-10,000				
118			100			1-10,000				
119			300			3-10,000				
120			300			3-10,000				
121		6.7	0			0				
122			0			0				
123			10			1-1,000				
124			10			1-1,000				
125			30			3-1,000				
126			30			3-1,000				
127			100			1-10,000				
128			100			1-10,000				
129			300			3-10,000				
130			300			3-10,000				

Sample ID	Sediment	pH	NOM (ppm C)	Tare Wt (g)	Tare + Sediment wt. (g)	NOM added (mL/Stock ppm)	Tube wt. after last pH adjustment	Added water to make equal vol. (mL)	Final Vol (mL)	Final pH
Procedure Step				1	2	4	9	10	11	13
131	Sand	3.9	0			0				
132			0			0				
133			10			1-1,000				
134			10			1-1,000				
135			30			3-1,000				
136			30			3-1,000				
137			100			1-10,000				
138			100			1-10,000				
139			300			3-10,000				
140			300			3-10,000				
141		5.3	0			0				
142			0			0				
143			10			1-1,000				
144			10			1-1,000				
145			30			3-1,000				
146			30			3-1,000				
147			100			1-10,000				
148			100			1-10,000				
149			300			3-10,000				
150			300			3-10,000				
151		6.7	0			0				
152			0			0				
153			10			1-1,000				
154			10			1-1,000				
155			30			3-1,000				
156			30			3-1,000				
157			100			1-10,000				
158			100			1-10,000				
159			300			3-10,000				
160			300			3-10,000				

Sample ID	Sediment	pH	NOM (ppm C)	Tare Wt (g)	Tare + Sediment wt. (g)	NOM added (mL/Stock ppm)	Tube wt. after last pH adjustment	Added water to make equal vol. (mL)	Final Vol (mL)	Final pH
Procedure Step				1	2	4	9	10	11	13
161	None	5.3	0			0				
162			0			0				
163			10			1-1,000				
164			10			1-1,000				
165			30			3-1,000				
166			30			3-1,000				
167			100			1-10,000				
168			100			1-10,000				
169			300			3-10,000				
170			300			3-10,000				

10.0 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; Data used in Figure 2).

Point of Zero Charge pH Testing --Blank				Point of Zero Charge pH Testing - Lysimeter				Labbook ID: ESE209, p3
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	

Tube	DH			DOH			DH-DOH		
	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 (used in K_d calculations).

CLIENT ID	Sediment	Target pH	DOC		Sediment Wt (g)	Rhenium (ug/L)	Selenium (ug/L)	Iodine (ug/L)
			Added (mg/L)	Final pH				
101	Clay	3.9	0	4.42	4.999	659	5	650
102	Clay	3.9	0	4.34	5.004	592	5	627
103	Clay	3.9	11	4.29	5	565	5	611
104	Clay	3.9	11	4.29	5	554	5	608
105	Clay	3.9	26	4.20	5.00	602	5	672
106	Clay	3.9	26	4.23	4.999	551	5	621
107	Clay	3.9	79	4.05	5.004	552	5	655
108	Clay	3.9	79	4.05	5.002	557	5	653
109	Clay	3.9	230	3.97	5	556	4.4	658
110	Clay	3.9	230	3.84	4.999	557	4.8	638
111	Clay	5.3	0	5.29	5.003	552	5	600
112	Clay	5.3	0	5.13	5	564	5	634
113	Clay	5.3	11	5.05	5.004	568	5	672
114	Clay	5.3	11	5.02	5.002	565	5	645
115	Clay	5.3	26	5.04	5.003	561	5	642
116	Clay	5.3	26	5.02	5.001	572	5	635
117	Clay	5.3	79	4.93	5.002	580	3.8	667
118	Clay	5.3	79	4.87	5	584	3	676
119	Clay	5.3	230	5.01	5.001	578	10.1	693
120	Clay	5.3	230	4.92	5.003	544	9.3	653
121	Clay	6.7	0	5.86	5.001	600	5	613
122	Clay	6.7	0	5.85	5.003	576	5	608
123	Clay	6.7	11	5.81	5	566	5	617
124	Clay	6.7	11	5.62	5.001	567	5	631
125	Clay	6.7	26	5.55	5.001	591	5	679
126	Clay	6.7	26	5.63	5.002	563	3.2	651
127	Clay	6.7	79	5.72	5.001	562	5.2	661
128	Clay	6.7	79	5.80	5.00	561	4.9	663
129	Clay	6.7	230	5.84	5.002	531	22.1	654
130	Clay	6.7	230	5.85	5.001	329	16.7	725
131	Sand	3.9	0	4.13	5.003	593	5	590
132	Sand	3.9	0	4.13	5.003	628	5	683
133	Sand	3.9	11	4.14	5.002	588	5	640
134	Sand	3.9	11	4.09	5.002	571	5	651
135	Sand	3.9	26	3.99	5	595	3.3	671
136	Sand	3.9	26	3.99	5.001	578	3	692
137	Sand	3.9	79	3.87	5.002	574	10.2	658
138	Sand	3.9	79	3.95	5.004	556	11.2	637
139	Sand	3.9	230	3.86	5.001	546	28.3	627
140	Sand	3.9	230	3.85	5.003	612	31	672
141	Sand	5.3	0	5.20	5.00	575	3.3	630
142	Sand	5.3	0	5.27	5.002	618	5	654
143	Sand	5.3	11	5.25	5.001	592	4.2	645
144	Sand	5.3	11	5.20	5.00	607	3.3	665

CLIENT ID	Sediment	Target pH	DOC		Sediment Wt (g)	Rhenium (ug/L)	Selenium (ug/L)	Iodine (ug/L)
			Added (mg/L)	Final pH				
145	Sand	5.3	26	5.34	5.001	568	4	674
146	Sand	5.3	26	5.13	5.004	592	5.4	682
147	Sand	5.3	79	5.16	5.001	615	25.5	692
148	Sand	5.3	79	5.15	5.002	588	23.9	654
149	Sand	5.3	230	5.18	5.001	534	60.6	610
150	Sand	5.3	230	5.22	5.003	592	70.7	635
151	Sand	6.7	0	6.51	5.003	589	9.3	611
152	Sand	6.7	0	6.57	5.002	567	8	621
153	Sand	6.7	11	6.44	5.001	570	10.9	648
154	Sand	6.7	11	6.45	5.002	588	11.7	658
155	Sand	6.7	26	6.51	5.001	588	29.4	651
156	Sand	6.7	26	6.34	5.002	621	23	690
157	Sand	6.7	79	6.34	5.003	559	61.7	627
158	Sand	6.7	79	6.49	5.002	566	83.1	609
159	Sand	6.7	230	6.30	5.00	569	103	613
160	Sand	6.7	230	6.28	5.002	563	101	617
161	None	5.3	0	5.31	0	562	582	621
162	None	5.3	0	5.25	0	597	603	630
163	None	5.3	11	5.47	0	569	598	636
164	None	5.3	11	5.47	0	589	622	642
165	None	5.3	26	5.37	0	583	588	605
166	None	5.3	26	5.33	0	556	571	608
167	None	5.3	79	5.45	0	550	611	626
168	None	5.3	79	5.38	0	554	592	608
169	None	5.3	230	5.40	0	582	619	622
170	None	5.3	230	5.31	0	563	594	549

Table A 4. Titration curve data for the sandy and red-clay sediments (Data used in Figure 3).

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.

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