Colloid and Ionic Tracer Migration within SRS Sediments: Final Summary (U)

by

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FINAL SUMMARY**

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CHAPTER I: EXECUTIVE SUMMARY

The generation of a stable colloidal suspension in geologic materials has a number of environmental implications. Mobile colloids may act as vectors for the transport of adsorbed contaminants through soils and within aquifers (McCarthy and Zachara, 1989) and can cause serious problems related to well monitoring and formation permeability in an injection well system (Vinten et al., 1983; O'Hare et al., 1986). Colloid-facilitated transport has been implicated in the migration of contaminants from seepage basins on the Department of Energy's Savannah River Site (SRS) at a rate greater than was predicted in two-phase transport models (Looney et al., 1987). From 1955 to 1988, seepage basins overlying the water-table aquifer received acidic wastes containing high levels of Na^+ and nitric acid, as well as trace radionuclides and metals from the nuclear materials processing facilities. Numerical simulations predicted that metal contaminants would not reach the water table, but measurable quantities of these contaminants have been detected in monitoring wells down gradient from the basins. Lack of agreement between predicted and observed contaminant migration in this and other studies has been attributed to both local nonequilibrium situations (Reardon, 1981), preferential flow paths within the geologic material, and to transport of the contaminant in association with a mobile solid phase, i.e. dispersed colloids (Looney et al., 1987; Newman, 1990; Newman et al., 1993; Kaplan, 1993). Additionally, the association of contaminants with a mobile colloidal phase has important ramifications for groundwater sampling on SRS intended to evaluate the potential environmental hazards of a given contaminant (Park, 1993, Clark et al., 1991).

As part of the F- and H-Area reclamation project, the Department of Energy has proposed the capture and treatment of the contaminant plume followed by reinjection of the treated water into the water table and upper confined aquifers. Contaminated groundwater in Aquifer zone IIB₂ contains elevated levels of tritium and other radionuclides, as well as Pb, Hg, Cr, and Cd. Results of waste-water treatment studies indicated that a pH of between 6.5-8.5 was required for efficient actinide and heavy metal removal, and NaOH proved to be the most effective pH modifier (Bibler, 1991).

The compatibility of the treated water with the injection zone is important to any long-term operation of the proposed groundwater corrective action. Formation clogging resulting from the introduction of particulates with the injection fluid or the mobilization of native clays adjacent to the injection well has been found to be the major limiting factor encountered in injection well systems (O'Hare et al., 1986). Therefore, the treated water will be relatively high in dispersive Na^+ and have an elevated pH, and the large volumes require that the water be injected under relatively high flow velocities, enhancing the potential for the generation of a stable colloidal suspension.

Colloid Project Objectives

In addressing the potential for colloid generation and transport within SRS sediments, the primary objectives of the colloid project were as follows:

- (1) to characterize the mineralogy of the clay fraction present within the formations underlying the SRS;
- (2) to evaluate the physical and chemical factors (SAR, ionic strength, pH, hydraulics) controlling clay dispersion and stable colloid formation within the highly-weathered sediments underlying SRS, and the impact of these factors on formation permeability;
- (3) to develop and critically evaluate analytical techniques for the characterization of dilute colloidal suspensions generated in column studies or collected with groundwater samples;
- (4) to characterize the composition and mineralogy of the dispersive clay fraction generated in column experiments; and
- (5) to evaluate the influence of solution chemistry on the surface charge properties of the SRS sediments using various ionic groundwater tracers.

Predicting the potential impact of the proposed F- and H-Area reclamation project and explaining the mechanisms that may have caused enhanced contaminant movement from the seepage basins require a better understanding of the mineralogy and surface chemistry of the highly weathered sediments underlying the Savannah River Site. The summarized results contained in this report should be of utility to a number of individuals involved in groundwater studies on the SRS and may aid in the management of waste facilities where colloids are of interest as a facilitator of contaminant transport.

Mechanisms of Colloid Generation (Chapter II)

Column studies indicated that colloid generation within the highly weathered sediments present on SRS was controlled by several factors in addition to the Na^+ concentration of the pore solution (Chapter II; Strom et al., 1994). Mobile colloids were produced under two extremely different chemical regimes; one due to high Na^+ levels in conjunction with high pH, and a second due to low pH and polyvalent cation (M^{2+} , M^{3+}) interactions with the oxide phase (Strom et al., 1994). To avoid dispersion, wastewater treatment specifications were adjusted to fall within this zone of maximum stability, but the formation of mobile colloids under moderately low pH conditions has a number of important implications to the F- and H-Area reclamation project. At present, it is unclear if the aquifer will pass back through the region of stable colloid formation as the pH of the acidic plume increases due to reclamation efforts. Dispersion in regions down gradient from the injection zone may increase the level of groundwater contaminants present in monitoring wells; thus, complicating any evaluation of the effectiveness of the remediation project. Such an increase can result from the presence of facility related contaminants or, in some cases, by the presence of large amounts of colloidal solids containing typical background levels. Elevated levels of colloidal particulates could potentially clog contaminated zones of the aquifer, thus reducing the hydraulic conductivity of these regions and the effectiveness of the remediation efforts. Additionally, in cases where the contamination is substantially above background and related to the contaminant plume, enhanced colloidal mobility may be used as a potential remediation strategy to improve contaminant capture within the seepage basin.

plume; thus, reducing the duration of the remediation effort (McCarthy and Wobber, 1993).

Characterization of Mobile Colloids (Chapter III)

The dilute nature of the suspensions generated in column studies inhibited characterization using x-ray diffraction. However, the importance of pH in controlling colloid generation and the positive electrophoretic mobility displayed by colloids generated under moderately low pH conditions (pH 4-5) indicated that the variable charge minerals, such as Fe and Al oxides, were playing a major role in controlling the surface characteristics of the mobile colloids and the aquifer matrix.

Samples containing moderate amounts of Fe oxides that were generally consistent with the Fe oxide content observed in numerous cores of the water-table (IIB2) and upper regions of the first confined aquifer required a shift in the groundwater chemistry to induce dispersion. As reported earlier (Chapter II; Strom et al., 1994), an increase in effluent turbidity coincided with a decrease in effluent pH during the leaching of dilute CaCl_2 solutions. In contrast, effluent turbidity was generally not observed during the leaching of DI water or NaCl solutions. For one particular sample that had a relatively high Fe oxide content ($> 3\text{g Fe}/100\text{ g sample}$), effluent samples were turbid from the onset of leaching and turbidity decreased over the duration of injection for both the CaCl_2 and NaCl injection solutions, but consistent with previous observations the initial level of turbidity was lower and it decreased earlier in leaching for the NaCl treatment solutions than for the CaCl_2 solutions.

Electrophoretic mobility measurements of the stable suspensions produced at the onset of leaching or resulting from a decrease in effluent pH were positive, indicating that the colloids were positively charged. Electron microscopy, energy dispersive x-ray, and thermal gravimetric analyses confirmed that the mobile colloidal phase consisted primarily of sub-micron sized Al-rich goethite with varying amounts of crandallite, a calcium aluminophosphate mineral ($\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$), rather than the predominate layer silicate, kaolinite. Automated analysis techniques designed to reduce artifacts associated with operator control generally confirmed the mineral categories identified using conventional SEM analysis.

Ionic Tracer Migration (Chapter IV and Chapter V)

The non-conservative transport or retardation of anions (Br^- and Cl^-) that are generally considered to be non-reactive within most groundwater environments confirmed the importance of the Fe oxide coatings in controlling the surface charge properties of the SRS sediments. Repacked columns of the four differing strata were leached with tritiated ($\approx 200 \text{ pCi mL}^{-1}$) KBr solutions of varying ionic strengths (0.1-0.001 M) to illustrate the influence of mineralogy and experimental methodology on the transport of a "conservative" ionic tracer, bromide. In addition, solutions containing 0.001 N MgBr_2 or KBr were leached through the subsurface materials to illustrate the influence of carrier cation on the breakthrough of the tracer anion. Pore water velocities estimated by bulk density and mass flux were consistent with those estimated from tritium breakthrough. In contrast, Br^- breakthrough differed dramatically between the four materials and was significantly altered by experimental conditions (sample drying, carrier cation, ionic strength, etc.). Retardation of 0.001 M KBr varied from 0.94 for the surface soil to 2.15 for the subsurface materials and increased with increasing Fe oxide content. In the presence of the divalent cation (Mg^{2+}), Br^- was retarded to a greater degree for the subsurface samples than in the presence of K^+ . In contrast, oven drying the sample reduced the degree of Br^- retardation observed for the subsurface materials.

These results indicate that retardation can vary dramatically within materials of similar texture, mineralogy, and origin. The apparent conservative behavior of an ionic species under a given set of conditions (mineralogy, pH, ionic strength, scale size, predominant counter ion) does not automatically ensure that transport will remain conservative as these conditions are altered by changes in experimental design or unforeseen circumstances that are encountered at the field scale.

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CHAPTER II:
Chemical Controls on Colloid Generation and Transport
in a Sandy Aquifer

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ABSTRACT

Colloid generation and transport in a highly-weathered subsurface material from the Upper Coastal Plain (Aiken, SC) was controlled by factors other than the Na^+ concentration of the leaching solution. Repacked columns were leached with solutions of various Na^+ to Ca^{2+} and Mg^{2+} ratios. Following injection of the treatment solution, the columns were leached with deionized water (DIW). For the mixed cation solutions prepared from Cl^- salts, colloid generation occurred only when the treatment solution was replaced with DIW, but the level of effluent turbidity decreased with increasing Na concentration and increasing duration of exposure to the high Na solution. CaCl_2 solutions produced substantial mobile colloids during injection that coincided with a decrease in effluent pH. The mobile colloids possessed a positive electrophoretic mobility suggesting that the drop in pH during salt injection, thought to be the result of specific cation adsorption and Al exchange and hydrolysis, may enhance dispersion by increasing the positive surface charge on both the mobile colloids and the immobile matrix. These results suggest that even minor changes in groundwater composition can influence surface charge and colloid generation in an Fe-oxide dominated system.

Introduction

Stable colloidal suspensions can be generated in the subsurface by several mechanisms including; movement of colloids from the vadose zone, formation of colloidal-size precipitates, dissolution of binding agents, and ionic interactions that result in clay dispersion (1). Mobile colloids may act as a vector for the transport of adsorbed contaminants through soils and within aquifers (1) and can cause serious problems related to well monitoring and formation permeability in an injection well system (2,3). Several studies have shown that colloids can increase the mobility of

strongly sorbing contaminants such as radionuclides, transition metals, and hydrophobic organics (4,5,6), but approaches to predicting contaminant movement have often neglected the potential for colloid facilitated transport because little information is available on the occurrence or physicochemical characteristics of colloids in groundwater systems.

Facilitated transport has been implicated in the enhanced movement of metals in an aquifer from the Upper Coastal Plain of South Carolina (7,8,9). Over many years, seepage basins overlying the Barnwell aquifer (Aiken, SC) received waste water containing high levels of sodium and nitric acid, as well as trace radionuclides and various metals from a nuclear materials processing facility on the Department of Energy's Savannah River Site (SRS). Although numerical simulations predicted that contaminant metals would not reach the groundwater, measurable concentrations of these contaminants have been detected in monitoring wells down gradient from the basins (8). The lack of agreement between predicted and observed contaminant migration has been attributed to local nonequilibrium situations (10), preferential flow paths, and to transport of the contaminant in association with a mobile solid phase, i.e. dispersed colloids (7,8,9). In column studies using material from the same formations, Newman et al. (9,11) investigated the transport of trace metals in a mixed acidic waste (pH 2.3). Initial breakthrough of Pb, Cr, Cu and Ni coincided with an increase in effluent turbidity and subsequent analysis revealed that a portion of these metals were associated with the colloidal phase. Newman (11) also observed that colloid generation from these sediments was favored by high pH and Na⁺ levels in solution. These somewhat contradictory observations tend to suggest two mechanisms of colloid generation and stabilization are possible within these highly weathered sediments.

The negative influence of Na⁺ on the physical properties of soils and other unconsolidated geologic material has been studied extensively (12,13,14,15), and the "sodium adsorption ratio" (SAR) has been used to characterize the Na⁺ status, and thus, the dispersion hazard of irrigation water. The SAR for a solution is defined as,

$$SAR = \frac{[Na^+]}{\sqrt{\frac{[Ca^{2+} + Mg^{2+}]}{2}}}$$

with all components expressed in terms of meq L^{-1} (16). Though empirical in nature, this equation reflects the natural preference of the exchanger phase for higher valence cations and has been shown to correlate well with the degree of sodium saturation on exchange sites or the "exchangeable sodium percentage" (ESP). Reduced soil permeability associated with high SAR solutions has been well documented in numerous experiments (3,17,18).

In addition to the Na^+ content of the percolating solution, the mobility of colloidal suspensions through porous media is controlled by factors that influence the surface charge of the dispersed particles, as well as the immobile matrix. In oxide-dominated systems, the surface morphology and solution pH has a major influence on the surface properties of the exposed matrix. The point of zero net charge (PZNC) for a mixture of constant- and variable-charge minerals is the pH at which total net charge vanishes under a given set of solution conditions (19). In addition to pH, the specific adsorption of humic substances, high valent cations, and oxy-anions can influence both the magnitude and the sign of surface charge on variable charge surfaces (19,20,21). The colloidal stability of a clay mixture is a reflection of the net surface charge of the combined mineral surfaces, and when at the PZNC, mixed suspensions will tend to flocculate regardless of the SAR or the background electrolyte concentration (19). In batch dispersion experiments at moderate to low pH values, flocculation is facilitated by the edge to face bonding of clay minerals, as well as the bonding of negatively charged surfaces of constant charge mineral fractions to the positively charged Fe and Al oxide surfaces (22). In column studies, Fe and Al oxides have been shown to stabilize clay systems in the presence of high exchangeable sodium percentages (23,24). Additionally, high levels of exchangeable Al have been shown to increase the aggregation and permeability of smectitic soils (25). In contrast, the adsorption of humic substances and oxy-anions has been shown to increase the electrostatic or physical barrier to particle aggregation and inhibit edge-to-face association of clay minerals by reducing the surface positive charge on variable charge mineral surfaces (26,27,28).

In a natural setting, the micromorphology of the clay assemblage may influence the type of charge character that is expressed by the "exposed" matrix. Hendershot and Lavkulich (29) observed that small quantities of Fe oxide ($\approx 4\%$ by weight), acting as

surface coatings on (<0.25mm fraction) quartz, shifted the point of zero net charge from a pH below 3 to approximately 8.1, a value similar to that observed for the same Fe oxide in the absence of quartz. To a lesser degree, the same shift was observed for kaolinite in the presence of Fe oxide. Despite the influence of clay micromorphology in controlling the expression of surface charge, colloid transport experiments are often conducted using disturbed coarse size fractions or acid-washed quartz sand as analogs for subsurface aquifer matrices (11,30,31,32). In such studies, particle mobility is enhanced by factors that increase the electrostatic repulsion between the mobile colloids and the column matrix, but the failure of filtration theory to predict colloid mobility in geologic materials illustrates the importance of surface heterogeneity and variable charge minerals other than quartz in controlling physicochemical particle attachment (33).

As illustrated by Puls and Powell (30), finer-size fractions of aquifer sediments are often removed by investigators to enhance the detection of the model colloid or to increase the efficiency of particle breakthrough in column experiments. Despite the concentration of the coarse fraction (0.5-1 mm), Scholl and Harvey (31) observed that the movement of bacteria through samples from an aquifer in Cape Cod MA was significantly retarded by adsorption (43.5 %) onto oxyhydroxide surface coatings of the sandy matrix, despite the fact that bacteria have a PZC in the pH range of 2 to 4. When those coatings were removed by leaching the sand with oxalic acid, only 26.7% of the applied bacteria were retained within the column. Olson and Litton (32) found that the mobility of negatively charged microspheres through sand was enhanced by chemical pretreatments that removed surface contaminants that altered the charge properties of the quartz.

The objective of this study was to evaluate the impact of changes in groundwater composition on the generation and transport of colloids from the vadose zone and water-table aquifer underlying the SRS seepage basins. The sensitivity of these formations to changes in solute chemistry is critical in assessing the potential for facilitated transport of seepage basin contaminants and in predicting the impact of a proposed pump, treat, and reinject remediation strategy on colloid generation in subsurface environments.

Materials and Methods

Location, Sample Collection, and Storage. The Savannah River Site is located on the Aiken Plateau of the Upper Atlantic Coastal Plain and is bounded on one side by the Savannah River. One of the zones of injection for the treated waste water, the Barnwell formation, consists mainly of deep red, fine to coarse sands and clayey sands with interbeds of clay, sandy clay, and gravel. To avoid bentonite contamination and sample disruption associated with conventional drilling, bulk material was collected from a nearby deep erosional exposure of the Barnwell formation. The dried surface crust was discarded and a uniform moist sample was collected for the column studies. The pH and electrical conductivity (EC) of the sample was determined in 2:1 ratio (solution/sample) with deionized water (DIW). Particle-size distribution was determined by the micro-pipette method (34) and the sands were size fractionated by dry sieving.

X-Ray Diffraction. The clay fractions were dispersed by saturation with Na_2CO_3 (pH 10) and then separated by centrifugation (35). Clay mineralogies were determined by x-ray diffraction from 2 to $30^\circ 2\theta$ using Cu K α radiation and a Phillips Norelco diffractometer equipped with a graphite monochromator. Slide treatments consisted of Mg, Mg-ethylene glycol (Mg-EG), and K saturation, the latter of which was heat treated at 110, 300 and 550 °C prior to x-ray analysis. Semi-quantitative mineral estimates were made by observation of peak intensities of the different minerals. Exchangeable cations were extracted with 0.5 M BaCl_2 , and the extracts were analyzed by atomic-absorption spectroscopy for Na, Ca, Mg, K, and Al. Cation exchange capacity was estimated by summing the BaCl_2 extractable cations.

Column Methods. Column experiments were performed in 10 cm long plexiglass tubes with an interior diameter of 5 cm (Figure 1). Field moist sample was packed in columns to a uniform bulk density of $\approx 1.5 \text{ g cm}^{-3}$. A given repacked column was used for only one leaching treatment before the matrix was replaced with fresh material. Acid washed coarse ($>500 \mu\text{m}$) sand layers (1 cm in depth) were placed above and below the sample to reduce the potential for colloid generation by turbulent flow and distribute flow. The columns were oriented vertically and slowly saturated from the outlet with

deionized water ($< 0.25 \text{ mL min}^{-1}$). After saturation, the columns were turned horizontally and flow was initiated at a constant rate of 5 mL min^{-1} (Darcy velocity of $\approx 3.6 \text{ m d}^{-1}$) with deionized water for < 0.20 pore volumes prior to the initiation of the fluid treatment. The EC, pH and turbidity (NTU) (HF Scientific, Inc.) of the effluent were monitored continuously, and leachate fractions were collected for analysis of solution cations by atomic absorption spectrometry (Perkin Elmer, Norwalk CT). The pressure head was measured at the inlet of the column as an indicator of hydraulic conductivity (K) and column plugging. A 0-1 PSI pressure transducer (Omega Inc.) was attached to the column inlet and the output voltage was calibrated using a water column that was open to the atmosphere at the inlet of the column. Electrophoretic mobility and particle size measurements were performed on selected effluent suspensions using a Zetasizer 4 photon correlation spectrometer-laser doppler velocimeter (Malvern Instr. Ltd., Malvern England). Treatment solutions included two mixed-cation solutions: one with an SAR of 8.56 and a total equivalent concentration of 7.68 meq L^{-1} (150 mg Na L^{-1} , 15 mg Ca L^{-1} , and 5 mg Mg L^{-1}) and a second solution (250 mg Na L^{-1} , 15 mg Ca L^{-1} , and 5 mg Mg L^{-1}) with an SAR of 14.28 and an equivalent concentration of 12.04 meq L^{-1} . These solutions were derived from either SO_4^{2-} or Cl^- salts. In addition to the mixed cation solutions described above, various cation/anion combinations, ionic strengths ($0.0001\text{-}0.1 \text{ M}$) and pH levels ($\approx 3.0, 5.6, 8.5, 10.0$) of leaching solutions were evaluated in terms of colloid generation. Treatments consisted of leaching the column for a prescribed number of pore volumes, in most cases 10, with a treatment solution followed by leaching with DIW to simulate dilution within the aquifer from low ionic strength native groundwater. All trends with respect to effluent chemistry and colloid generation were confirmed with at least two treatment replications using fresh matrix material.

Results and Discussion

Sample Characterization. The mineralogy of the clay fraction consisted primarily of kaolinite, goethite and mica (illite). Similar clay mineralogy was observed in previous studies for corings throughout the Barnwell aquifer (36). Due to the coarse texture of the material and the low reactivity of the clay fraction, the sample possessed a low cation exchange capacity (Table 1), $\approx 85\%$ of which was satisfied by exchangeable Al

(0.53 cmol(+) kg⁻¹). The remaining exchangeable cations accounted for < 0.1 cmol(+) kg⁻¹, and the exchangeable sodium percentage (ESP) for the material was less than 1%. Magnesium was the only cation other than Al that accounted for an appreciable amount of the exchange capacity ($\approx 12\%$).

Table 1. Physical and chemical characteristics of sample used in column experiments.

cation	$\text{cmol}_{(+)} \text{kg}^{-1} \times 10^3$	$\text{SD}^b \times 10^3$
Na	2.4	0.4
Ca	14.7	1.2
Mg	72.1	6.7
K	5.8	0.6
Al	530	63
CEC ^c	625	72
ESP ^d	0.38	0.03
ex. Al %	84.8	0.037
	$\text{g } 100 \text{ g}^{-1}$	SD^b
Sand	90.6	1.3
Silt	1.3	1.3
Clay	8.2	2.0
Sand Fractionation		
>1mm	7.9	
>500 μm	24.5	
>250 μm	27.5	
>106 μm	40.5	
>53 μm		
<53 μm		
1:2 soil to solution ratio		
pH_{water}	4.94	0.04
pH_{KCl}	4.42	0.07
$\text{EC}_{\mu\text{S/cm}}$	5.47	0.49

^aExtractable in 1N BaCl₂^bStandar Deviation^cSum of Extractable Cations^dExtractable Na Percentage

Column Results

No significant effluent turbidity (<1 NTU) was observed for columns leached exclusively with DIW, indicating that colloid generation was controlled by solution chemistry and not an artifact of the disruptive influence of sampling and column packing. Effluent turbidity remained extremely low (< 1 NTU) during the leaching with the mixed cation solutions, even after prolonged exposure (>50 PV) (Figure 2.). The turbidity did, however, increase when DIW was introduced through these columns, corresponding to a reduction in the ionic strength of the column effluent. The excellent agreement of the turbidity measurements for the replicate treatments (10 PV mixed cation solution) illustrates the high degree of reproducibility observed for the column results. Surprisingly, the degree of colloid generation decreased both with increasing Na^+ concentration and with increasing duration of exposure to the high SAR solutions. Over a pH range of 5 to 10, the degree of dispersion expressed when the treatment solution was replaced with DIW decreased with increasing pH (data not shown). The dispersibility of the column would be expected to increase with extended exposure to the high SAR solution, unless the matrix had a higher native exchangeable sodium percentage (ESP) than the level promoted by the treatment solution. This was not the situation in the present study because the sample had a very low native ESP and a high degree of Al saturation ($\approx 85\%$), suggesting that Na^+ was not responsible for the observed dispersion when the mixed cation treatment solutions were replaced by DIW. Additionally, no significant change in hydraulic conductivity (data not shown) resulted from the generation of dilute suspensions in this study, suggesting that solution chemistry and surface charge on the dispersed phase and the column matrix, rather than physical filtration, were the primary factors controlling particle generation and capture within the column.

Influence of Solution Cation on Colloid Generation. To separate the influence of Na^+ and Ca^{2+} on colloid generation, solutions composed of either 6.5 meq L^{-1} NaCl (150 mg Na L^{-1}) or CaCl_2 ($\approx 130 \text{ mg Ca L}^{-1}$) were introduced to the columns for 10 pore volumes followed by several pore volumes of DIW. Based on the SAR values of the influent solutions, the NaCl solution ($\text{SAR} \infty$) should have induced the greatest level of

clay dispersion; however, the CaCl_2 solution (SAR 0) treatment became turbid within the first two pore volumes following injection and slowly cleared until the solution was replaced with DIW after 10 pore volumes of leaching (Figure 3A). The switch to DIW resulted in a second pulse of turbidity, but to a lesser extent than was expressed for the mixed cation treatment. Surprisingly, the Na^+ effluent was never turbid, even when DIW was introduced into the column following injection of 10 pore volumes of the Na solution, suggesting that the Na^+ in the mixed cation treatment solution may have inhibited the initial colloid dispersion and transport observed for the CaCl_2 injectate. As previously noted, effluents from the mixed cation treatments (150 mg Na L^{-1} , 15 mg Ca L^{-1} , and 5 mg Mg L^{-1} as Cl^- salts) were turbid only following leaching with DIW. These results confirm that factors other than Na^+ levels were controlling clay dispersion in the column system.

The greatest initial decrease in column effluent pH (to $\approx \text{pH } 4.0$) was observed for the CaCl_2 treatment solutions (Figure 3B). This pH decrease corresponded quite closely with the initial pulse of turbidity in the CaCl_2 treatment (Figure 3A). After the initial decrease, the effluent pH increased only moderately over the course of leaching, but then increased to about 5.0 after the CaCl_2 solution was replaced with DIW. The NaCl injection solution resulted in the smallest change in effluent pH of the treatment solutions studied and also displayed the highest effluent pH when the solution was replaced with DIW. The mixed cation solution resulted in an intermediate pH, but with continued injection, the pH decreased gradually to a value similar to that observed for the CaCl_2 treatment following injection of DIW. The higher pH observed in the Na^+ treatments may result from the ineffective exchange of Na^+ with Al^{3+} on the exchange complex of the column matrix (37). In the mixed cation solutions, the levels of Ca^{2+} (15 mg L^{-1}) and Mg^{2+} (5 mg L^{-1}) were adequate to promote Al^{3+} exchange and hydrolysis with extended leaching, which resulted in a similar decrease in pH to that observed in the CaCl_2 treatment.

Electrophoretic Mobility and Particle Size. Particle size and electrophoretic mobility were determined for colloids generated in selected column treatments. Electrophoretic mobility of the column suspensions is a better indicator of net surface

charge under the conditions responsible for colloid stabilization than potentiometric titrations, because it is insensitive to errors resulting from altering the ionic strength and composition of the bathing solution. Colloids generated in the column experiments displayed a positive electrophoretic mobility (Table 2). There was some variability in particle size, but in general, size ranged from about 400-660 nm. Newman et al. (9,11) failed to characterize the electrophoretic mobility for the colloids generated in heavy metal leaching studies using sediments from the same aquifer, but the particle size and surface charge of the colloids in the present study were consistent with mobile colloids collected from an acidic contaminant plume within the Barnwell aquifer that have been implicated in the transport of Cr, Ni, Cu and Pb (7).

Table 2. Properties of colloids generated during column experiments.

Column Treatment	Particle Size			Electrophoretic Mobility	
	(nm)	(+/-)		($\mu\text{m/s}$)/(V/cm)	(+/-)
mixed cation (10PV) ^a sample ^b 1	(A) ^c	474	33	+2.67	0.11
mixed cation (10PV) sample 2	(A)	499	18	e	
mixed cation (10PV) rep ^d 2	(A)	462	32	+2.90	0.1
sample 1					
mixed cation (10PV) rep 2	(A)	419	5	e	
sample 2					
mixed cation (25PV)	(B)	666	26	+1.95	0.17
mixed cation (50PV) sample 1	(C)	416	11	e	
mixed cation (50PV) sample 2	(C)	412	19	e	
0.001 N CaCl ₂ (10PV)	(D)	e		+2.40	0.11

^aDuration of injection prior to switching to DI water

^bSubsamples from same column

^cLetters refer to turbidity pulses displayed in Figures

^dReplications in separate columns

^eNot determined

Influence of Anions on Colloid Generation. The influence of various anions on dispersion was determined by leaching columns with equivalent (6.5 meq L^{-1}) solutions of various Na^+ and Ca^{2+} salts. Consistent with the Schulze-Hardy Rule of colloid stability for a positively-charged phase (19), the sulfate salts of Ca^{2+} and Na^+ failed to produce mobile colloids during leaching (Figure 4), or when replaced with DIW. Production of mobile colloids was also inhibited by the introduction of a $\text{Ca}(\text{OH})_2$ solution, confirming the importance of the downward shift in pH for colloid generation.

As previously noted for other concentrations of Na^+ , solutions ranging from 0.001 to 0.1 M were ineffective at creating a stable suspension during injection or when followed by DIW (not shown). Of the solutions tested, CaCl_2 appeared to be the most effective at generating a stable colloidal suspensions at low pH. The influence of Ca^{2+} concentration on colloid generation was evaluated by leaching columns with CaCl_2 solutions ranging from 0.001-0.1 N. In addition to the varying concentrations, the 0.001 N solution treatment was repeated with a solution in which the pH had been adjusted to 3.08 by addition of HCl. To differing degrees, both the initial pulse of turbidity and the turbidity pulse following the introduction of DIW was observed for each of the CaCl_2 treatments (Figure 5A). The highest ionic strength treatment displayed the lowest initial turbidity during the early phase of leaching (i.e., the first few pore volumes), but the turbidity for this treatment was the highest when DIW injection was initiated. The 0.001 N CaCl_2 solution with an adjusted pH of ≈ 3.0 resulted in the lowest effluent pH (Figure 5B) and maintained elevated turbidity during the entire duration of injection, indicating that the stability of the mobile colloids could be maintained even at higher ionic strength, if the pH was low enough. When the acidified CaCl_2 solution was replaced with DIW, the turbidity of the column effluent initially increased and then cleared as the pH of the effluent solution began to increase.

Mechanism of Colloid Generation. At low ionic strengths that are more analogous to the native groundwater conditions ($<0.1 \text{ M}$), neither cations nor anions were transported conservatively. Solute breakthrough in these highly weathered sediments was dependent on the identity of both the cation and anion involved, indicating that the expression of net surface charge was sensitive to minor changes in

solution composition (36). The retardation of anions attributable to an increase in concentration dependent charge on the Fe oxide fraction should result in a pH shift towards the PZC of the sorbing mineral (38). Instead of an upward shift in pH, injection of the NaCl solution induced little change in pH over the course of leaching, while the CaCl_2 injectate reduced the effluent pH (Figure 6A). These results suggest that reactions other than simple equivalent exchange of cations and ionic strength dependent adsorption of anions occurred within the column.

Colloidal suspensions generated from the mixed cation and Ca^{2+} solutions appear to be the result of both hydrolysis reactions of exchanged Al (Figure 7A) and specific adsorption reactions of divalent cations (Figure 7B); thus, lowering solution pH, increasing net-positive surface charge, and reducing exchange equivalency of any released Al species. Reactions A and B act as apparently non-equivalent sinks for both treatment solution cations and hydroxyls generated during concentration dependent adsorption of anions on variable charge surfaces below their PZC. Experimentally distinguishing between these two mechanisms based on bulk effluent solution data is difficult in systems containing both types of surfaces because the relative affinity of the cation to form more specific interactions with the oxide surface roughly corresponds to the ability of the cation to replace exchangeable Al. In addition, the tendency of Al hydrolysis products to precipitate or readsorb, especially on kaolinite, makes it difficult to perform adequate charge or mass balance estimates based on effluent solution data (39,40).

Even though Fe and Al oxides possess a net positive charge under the initial pH conditions of the column system ($\text{pH} \approx 5.0$), a reduction in pH was required to increase the positive charge on the exposed matrix until net charge reversal occurred and the system fell below the PZNC for the combined mineral assemblage, insuring that positively charged mobile colloids would not be recaptured within the column. As observed at other concentrations, CaCl_2 (1 meq L^{-1}) was effective at generating turbidity that coincided with an initial decrease in effluent pH (Figure 6). A second pulse of turbidity was observed when the solution was replaced by DIW, but the effluent cleared as Ca^{2+} was leached from the column and the pH began to increase (Figure 6A). Even when positively charged at pH values below the PZC, Fe and Al oxides

retain a high affinity for polyvalent cations via specific adsorption, especially alkaline earth and transition metals (41,42), and this adsorption has been shown to increase the surface positive charge of Fe oxides as measured by electrophoretic mobility (43). Because of the affinity of the column matrix for Ca^{2+} , the ionic strength breakthrough for the CaCl_2 treatment was delayed and the effluent EC remained lower for a longer period than was observed for the Na^+ containing solutions (Figure 8A). The apparent non-equivalent retardation of Ca^{2+} coincides with the downward shift in solution pH (Figure 6A) and the generation of the colloidal suspension (Figure 6B). In part, the discrepancy in charge balance may reflect the poor flame AA detection limits for Al that may have been displaced within the column and the greater ionic mobility of the resulting H^+ that accounts for the remainder of charge required to meet the condition of electrical neutrality. Magnesium was the primary cation displaced from the column and the equivalent amounts of Mg^{2+} , K^+ , and Na^+ detected in the effluent solution were consistent with those predicted from previous measurements of exchangeable cations (Table 1), indicating that Ca^{2+} was effective at removing essentially all of those exchangeable species. Consistent with the mechanism described above, the production of colloids declined as the pH of the effluent began to increase and excess Ca^{2+} was leached from the column. Summation of all major solution cations (other than Al and H^+) in the effluent accounted for approximately 94 % of the inlet treatment equivalents, suggesting a net adsorption of Ca^{2+} within the column. Most of this net adsorption can be accounted for by the delay in effluent breakthrough at the onset of leaching and the discrepancy between the sum of solution cation equivalents and the measured effluent EC. The high recovery rate for equivalent cations in the Ca^{2+} treatment was in part a function of the duration of the experiment. Most of the "apparent" discrepancy in charge balance resulted at the onset of the experiment and the extended leaching made it increasingly difficult to detect adsorption as the effluent began to approach the composition of the inlet solution.

For the NaCl solution, which failed to produce any significant mobile colloids, essentially all of the inlet solution equivalents ($\approx 101\%$) could be accounted for by summing the Na^+ , K^+ , Ca^{2+} and Mg^{2+} present in the column effluent (Figure 8B). In this case the cation breakthrough identically corresponded to the measured EC

breakthrough indicating that little if any net cation adsorption occurred within the column and that all of the reactions involved in solute retardation were reversible or could be accounted for by simple equivalent cation and anion exchange. In addition to controlling colloid generation, surface/solute reactions that influence the expression of surface charge on the aquifer matrix can affect the migration of ionic solutes/contaminants and the determination of physical transport parameters using ionic tracers such as bromide (36).

CONCLUSIONS

The results of this study and those of Kaplan et al. (44) suggest that the mechanisms of colloid formation and stabilization in unconsolidated geologic materials from the Upper Coastal Plain of the southeastern U.S. differ for surface and subsurface environments. In lysimeter studies using sandy surface horizons of the Blanton soil series (Grossarenic Paleudult), Kaplan et al. (44) characterized colloids generated under various flow regimes. At low flow rates the mobile colloidal fraction consisted primarily of goethite and gibbsite. Despite pH values below the reported PZCs for these minerals, the mobile colloidal fraction possessed a negative surface charge, illustrating the importance of organic coatings in controlling the surface properties of variable charge minerals in surface environments of this region.

In the subsurface environment, where the organic carbon content is very low, the oxide minerals appear to control the surface reactivity of the dispersed particles, as well as the immobile matrix. The movement of positively charged colloids is most often associated with acidic contaminant plumes (7), but the results of the present study indicate that matrix charge reversal can result from even minor changes in solute composition, i.e., cation/anion identity and valence, pH, and ionic strength. Colloid generation and transport can occur at an initially more neutral pH due to a combination of the following: specific cation adsorption, Al^{3+} exchange and hydrolysis reactions, and the appropriate mineral assemblage; both with respect to content and spatial arrangement. In addition to enhancing the mobility of sparingly soluble contaminants, the positively-charged colloidal phase is likely to increase the concentration of native metals measured in unfiltered groundwater samples taken from monitoring wells.

Research into the mechanisms of colloidal generation and transport has focused primarily on the dispersive influence of high pH, Na⁺, and oxy-anions, as well as low molecular weight organics. Most groundwater matrices are viewed as having a net negative surface charge; therefore, column experiments are often biased towards factors that enhance the movement of negatively charged colloids through a negatively charged matrix. This approach may be valid in systems that contain appreciable quantities of high charge clays or where organic coatings control surface charge expression, but it may overlook low pH mechanisms of colloid stabilization and transport in more highly weathered oxidic systems typical of the Atlantic Coastal Plain Sediments. Extremely disturbed (drying/grinding) geologic materials are often saturated with high ionic strength solutions of a given SAR in an attempt to have a greater control over the factors that influence colloid generation, thus overlooking the initial dynamic interactions of an altered groundwater chemistry, including the reactions of Al³⁺ exchange and hydrolysis, with a spatially distributed mineralogy. Also, without surface charge characterization of the mobile phase, e.g., electrophoretic mobility, dilute colloidal suspensions produced in column experiments may be incorrectly attributed to factors such as column packing, native Na levels, or dissolution of cementing agents.

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Figure 1. Schematic diagram of experimental column setup. The pressure drop along the column and the effluent pH, turbidity, and electrical conductivity (EC) were monitored continuously using a PC.

Figure 2. Effluent turbidity during extended leaching with mixed cation solutions followed by DI water (DIW). Numbers in parenthesis refer to the duration of leaching with the mixed cation solution prior to leaching with DIW and letters refer to particle size and electrophoretic mobility data in Table 2.

Figure 3. Effluent turbidity (A) and pH (B) during leaching of mixed cation, CaCl_2 (≈ 3.3 mM), and NaCl (≈ 6.5 mM) solutions for 10 pore volumes followed by DIW.

Figure 5. The impact of ionic strength on effluent turbidity (A) and (pH) of various CaCl_2 solutions during leaching and when replaced with DIW.

Figure 6. The impact of 0.001 N CaCl_2 and NaCl on effluent pH (A) and turbidity (B).

Figure 7. A schematic representation of the mechanisms responsible for the shifts in effluent pH and the generation of positive charge on the mobile colloids and the stationary matrix.

A. Al Exchange and hydrolysis

B. Specific Cation/Oxide Interactions

C. pH Dependent Charge Development

Figure 8. Effluent charge and mass balance estimates for the breakthrough of 0.001 N CaCl_2 (A) and NaCl (B).

CHAPTER III:**Mineralogy and Composition of Mobile Colloids from a Highly Weathered Sediments Present on SRS**

To be submitted to Clays and Clay Minerals.

ABSTRACT

Two subsurface samples representing the highly-weathered sediments of the Upper Coastal Plain (Aiken, SC) were subjected to various drying regimes prior to conducting leaching experiments to evaluate the impact of various dilute salt solutions on the generation of mobile colloids. The bulk clay fraction of both materials, as identified by XRD, consisted primarily of kaolinite, goethite, mica and crandallite, but the two samples differed in total Fe oxide content. Field-moist samples were uniformly packed into 10 cm long plexiglass columns (ID 5 cm) and leached (≈ 3.6 m d⁻¹ Darcy vel.) with either 0.001 N NaCl or CaCl₂ solutions for 10 pore volumes followed by 10 pore volumes of DI water. The low Fe oxide content sample displayed an increase in effluent turbidity that coincided with a decrease in effluent pH during the leaching of the CaCl₂ solutions. In contrast, no effluent turbidity was observed during the leaching of NaCl solutions. The Fe oxide enriched sample displayed greater effluent turbidity from the onset of leaching. The turbidity decreased over the duration of injection for both the CaCl₂ and NaCl injection solutions, but the initial level of turbidity was less and decreased faster for the NaCl treatment solutions. Electrophoretic mobility of the stable turbid suspensions indicated that the colloidal phase possessed a net positive surface charge. Electron microscopy, energy dispersive x-ray and thermal gravimetric analysis confirmed that the mobile colloidal phase consisted primarily of sub-micron sized Al rich goethite with varying amounts of crandallite, rather than the predominate layer silicate, kaolinite.

INTRODUCTION

Several recent studies have reported the unattenuated transport of colloidal-size particulates in soils and coarse textured groundwater matrices (Gschwend and

Reynolds, 1987; Ryan and Gschwend, 1990; Kaplan, et al. 1993). Mobile solid phases can facilitate the transport of strongly sorbing contaminants such as radionuclides, transition metals, and hydrophobic organics (McCarthy and Zachara, 1989). In many cases where elevated levels of mobile particulates have been observed, interactions of the Fe oxide minerals with an altered solution chemistry associated with groundwater contamination has been implicated in controlling enhanced colloid generation and stabilization (Gschwend and Reynolds, 1987; Ryan and Gschwend, 1990; Newman et al., 1993). Colloidal ferrous phosphates have been found to precipitate beneath recharge basins due to changes in groundwater redox potential associated with an increase in organic carbon (Gschwend and Reynolds, 1987). In another study, Ryan and Gschwend (1990) attributed the differences in the colloid concentration (60 vs 1 < mg/L) present in adjacent wells within the same formation to differences in redox potential that increased the solubility of Fe oxides that had acted as cementing agents.

The primary factors controlling the dispersion of colloidal material from the soil or aquifer matrix are the mineralogy and surface chemistry of the colloidal size fraction, as well as the pH, ionic strength, and chemical composition of the pore solution. As observed by Ryan and Gschwend (1990), Fe oxides are usually considered to act as stabilizing agents in soils and sediments (Schwertmann and Taylor, 1989; Goldberg and Glaubig, 1987), and therefore are not considered to be extensively mobile in the environment (Vilks et al., 1993). When Fe oxides are found to be mobile in the environment they are often associated with adsorbed organic matter that results in a negative surface charge. Ryan and Gschwend (1990) found that approximately 50 % of the organic carbon collected from the anoxic wells was adsorbed to the solid phase, increasing both the steric and electrostatic stability of the mobile colloids. In lysimeter studies using sandy surface horizons of the Blanton soil series (Grossarenic Paleudult), Kaplan et al. (1993) characterized colloids generated under various flow regimes. At low flow rates associated with flux through smaller soil pores, the mobile colloidal fraction consisted primarily of submicron goethite and gibbsite particles. Despite pH values below the reported PZCs (Point of Zero Charge) for these minerals, the mobile colloidal fraction possessed a negative surface charge that was attributed to organic coatings. Similarly, Liang et al. (1993) observed that the oxidation of reduced

groundwater rich in organic matter resulted in the formation of organically coated Fe oxides that displayed negative electrophoretic mobilities.

From 1955 to 1988, seepage basins overlying a sandy aquifer on the Department of Energy's Savannah River Site (Aiken, SC) received acidic waste water containing high levels of sodium and nitric acid, as well as trace radionuclides and various metals. Numerical simulations predicted that contaminant metals would not reach the groundwater for many years, but measurable concentrations of these contaminants have been detected in monitoring wells down gradient from the basins. The enhanced transport of contaminant metals has been attributed to local nonequilibrium situations (Reardon, 1981), preferential flow paths, and to transport of the contaminant in association with a mobile solid phase, i.e. dispersed colloids (Kaplan, 1993; Looney et al., 1987; Newman et al., 1993).

The dilute nature of most groundwater suspensions has hindered the characterization of the mobile solid phase, but energy dispersive x-ray analysis (EDX) in conjunction with electron microscopy has been used by many investigators to characterize the mineralogy and chemical composition of dilute colloidal suspensions collected from aquifers (Bucholtz ten Brink et al., 1993; Gschwend et al., 1990; Gschwend and Reynolds, 1987; Ronen et al., 1992; Vilks et al., 1993) or generated in repacked column studies (Newman et al., 1993). Based on SEM/EDX spectra, Kaplan et al. (1994) were able to place the mobile colloids collected from the water table aquifer down gradient from an acidic seepage into one of four categories: (i) a phase containing only Si that was identified as quartz, (ii) an aluminosilicate phase containing an appreciable amount of K that was attributed to mica or hydroxy-interlayered vermiculite, (iii) an aluminosilicate that contained approximately a 1:1 ratio of Si to Al that was identified as kaolinite, and (iv) a Ti rich Fe-oxide phase. Similar mineral classes of mobile colloids were also observed by Ryan and Gschwend (1990) for two Atlantic Coastal Plain aquifers in New Jersey. Because of the poor sensitivity of EDX analysis, Kaplan et al. (1994) were unable to detect any of the seepage basin contaminants thought to be associated with the mobile colloid phase, but synchrotron X-ray fluorescence (SXRF) analysis of the same particles revealed that Cr, Ni, Cu, and Pb were associated almost exclusively with the Ti-rich Fe oxide phase.

In contaminant transport studies using repacked columns of aquifer material representative of the mineralogy found beneath the Savannah River Site seepage basins (Barnwell/Tobacco Rd. Formation), Newman et al. (1993) observed that the breakthrough of Pb, Cr, Cu and Ni from an acidic mixed waste ($\text{pH} \approx 2.3$) coincided with an increase in effluent turbidity. In contrast to these results, Newman (1990) also observed that colloid generation from these sediments was favored by high pH and Na solutions. These somewhat contradictory observations tend to suggest two mechanisms of colloid generation and stabilization are possible within these highly weathered sediments. Subsequent SEM/EDX analysis revealed evidence that a portion of the contaminant metals were actually adsorbed to the colloidal phase, but the authors (Newman et al., 1993) failed to indicate if the filters were rinsed to remove any soluble or weakly sorbed contaminants prior to analysis. Based on the same SEM/EDX analysis, Newman (1990) separated the mobile colloids into one of three categories according to morphology: 1) clay platelets of 5 to 10 μm in diameter, 2) distinctly rod-shaped particles of approximately 5 μm in length, and 3) the more common spherical particles of approximately 0.1 μm in diameter. Even though Newman (1990) observed a similar degree of turbidity over a wide range of flow velocities, the large particle size observed for two of the fractions and the instability that the authors noted for the turbid suspensions suggests that a significant fraction of the dispersion may be an artifact of the experimental methodology and not representative of colloids that are truly mobile within the aquifer.

In another set of column experiments, Seaman et al. (Chapter II) observed that dilute colloidal suspensions were generated when the highly weathered sediments of the Barnwell/Tobacco Rd. formation (Aiken County, SC) were leached with solutions of divalent chloride salts (e.g. CaCl_2 , MgCl_2). A continuously dispersed dilute suspension was created when these solutions were acidified with HCl ($\text{pH} 3.0$), but high Na/Ca ratios or the presence SO_4^{2-} in the treatment solution reduced or inhibited colloid production. Suspensions generated in the column experiments appeared generally stable and a significant portion failed to flocculate over several weeks of storage. Electrophoretic mobility measurements indicated that the colloids possessed a net positive surface charge and Seaman et al. (Chapter II) suggested that the decrease in

pH accompanying the leaching of divalent salts and the specific interactions of the oxide surface with the divalent cations increased the positive surface charge on both the mobile colloids and the Fe-oxide coated matrix. Based on the positive electrophoretic mobility and the high goethite content of the aquifer sediments, Seaman et al. (Chapter II) assumed that the mobile colloids consisted predominately of Fe oxides, but identification of the mineralogy by XRD was impractical because of the dilute nature of the suspensions.

The objective of this study was to characterize mobile colloids generated in column leaching experiments using the highly weathered sediments of the Upper Coastal Plain (Aiken County, SC) with respect to chemical composition and mineralogy. SEM/EDX analysis was used to place the mobile colloids into general categories and to quantify their distribution between these categories. Transmission electron microscopy (TEM) combined with EDX and selective area diffraction (SAED) was used to support or confirm the mineralogical designations observed during SEM analysis.

EXPERIMENTAL METHODS

Sample Collection and Characterization

Two Fe oxide rich sands were collected from a deep erosional exposure of the Barnwell/Tobacco Rd. formation on the Savannah River Site (Aiken, SC). Prior to sample collection, the dried surface crust and overburden present on the exposure was removed to reveal the moist homogeneous material. For identification, the clay fractions of the bulk samples were dispersed by saturation with Na_2CO_3 (pH 10) followed by overnight shaking, then separated by centrifugation (Jackson, 1979) and concentrated by the addition of MgCl_2 . Aliquots of the clay concentrates were plated on petrographic slides using the Drever method (1973), and clay mineralogies were determined by x-ray diffraction from 2 to $30^\circ 2\theta$ using Cu K α radiation and a Phillips Norelco diffractometer equipped with a graphite monochromator. Total free Fe oxide contents for the bulk samples were measured by citrate-dithionite-bicarbonate (CDB) extraction (Mehra and Jackson, 1960) and amorphous Fe oxide content was estimated by ammonium oxalate (AO) extraction in the dark (Jackson, 1979) using Atomic Absorption Spectrometry (AAS) for Fe determination. To improve characterization, the clay mineralogy of the

bulk clay fraction was compared to that of the sample with the Fe oxides removed by CDB extraction (Mehra and Jackson, 1960). Slide treatments consisted of Mg, Mg-ethylene glycol (Mg-EG), and K saturation, the latter of which was heat treated at 110, 300 and 550 °C prior to x-ray analysis.

Sample Treatment

The column experiments were performed in 10 cm long plexiglass tubes with an interior diameter of 5 cm as described by Seaman et al. (Chapter II). Briefly, field moist sample was packed in columns to a uniform bulk density of $\approx 1.5 \text{ g cm}^{-3}$. Above and below the sample, sand layers (1 cm in depth) were included to disperse flow throughout the entire cross section of the column and to reduce the impact of turbulent flow on colloid formation. The repacked columns were then slowly saturated from the outlet with deionized water (DI), oriented horizontally, and leached at a Darcy velocity of $\approx 3.6 \text{ m d}^{-1}$ for 10 pore volumes with the appropriate treatment solution, followed by several pore volumes of DI water. Solution treatments consisted of 0.001 N NaCl or CaCl₂. The pH, electrical conductivity (EC), and turbidity of the column effluent was continuously monitored, and turbid samples were collected for surface charge and chemical characterization. A given repacked column was used for only one leaching treatment before the matrix was replaced with fresh material.

The influence of sample drying on the generation of colloids in column leaching experiments was observed by subjecting a portion of the two bulk samples to one of three treatments: i) air-drying plus sample disruption, ii) air-drying without sample disruption, and iii) oven-drying (OD) overnight at 110°C. These three treatments were compared to the conservative practice of storing the sample in a field moist state at 4 °C until column packing. The air-drying plus sample disruption treatment consisted of allowing sample to dry in the lab for three days and then vigorously homogenizing the sample prior to column packing. This treatment represented the conventional practice of air-drying and sieving a sample prior to conducting analysis or column packing. The air drying without sample disruption treatment consisted of packing the field-moist sample into the column, attaching an air pump to the column outlet with tygon tubing,

and purging the sample overnight with dry air to minimize any physical sample disruption.

Colloid Analysis

The electrophoretic mobility of selected colloidal suspensions produced in the column experiments was determined using photon correlation spectrometry with laser doppler velocimetry (Delsa 440, Coulter Electronics). Scanning electron microscopy (SEM), combined with energy-dispersive x-ray spectrometry (EDX), was used to identify the general mineralogy and bulk chemical composition of the turbid suspension, because insufficient colloidal material was collected for conventional x-ray diffraction (XRD) analysis. Transmission electron microscopy (TEM) and Selective Area Electron Diffraction (SAED) were performed to further classify the mineralogy of the major components and to confirm the general mineral classes established by SEM analysis. For comparison, three synthetic goethites and a reference kaolinite (Ga-2, Source Clay Minerals Repository) were analyzed by SEM/EDX and thermal gravimetric analysis (TGA). The goethite standards consisted of one pure goethite and two Al-substituted goethites consisting $\approx 6\text{-}10\%$ Al substitution as described by Schwertmann and Cornell (1991).

Selected samples of the suspensions generated in the column experiments were immediately filtered through $0.1\text{ }\mu\text{m}$ pore size polycarbonate filters. After 2-5 mL of the suspension had been deposited on the filter, an additional 5-10 mL aliquot of deionized water was filtered through the sample to remove any soluble salts that may have accumulated with the particles. A 5 mm x 10 mm portion of the filter was secured with carbon tape to an SEM stub and coated with evaporated carbon prior to EDX analysis. Filters were observed with a Hitachi S 800 SEM equipped with a field emission gun for higher resolution and a Tracor 5500 EDS system for compositional analysis (Tracor Northern Inc.). In the SEM, the field emission gun provides the best resolution for imaging and microanalysis for sub micron size particles (Williams et al., 1986). Carbon coated filters were systematically scanned and EDX was performed randomly on approximately 20 to 25 particles or small aggregates of particles per filter. Selected micrograph images were taken of representative particles on the carbon-coated filters,

but the resolution was inadequate to accurately assess aggregate size or primary particle morphology. After the EDX analysis was completed, the filters were Au-Pd coated for better resolution and photomicrographs were taken of representative regions of the filters.

Automated SEM Analysis

Automated analysis was conducted using a JEOL JSM 6400 scanning electron microscope (JEOL Inc., Peabody MA) controlled by a Noran Voyager energy dispersive x-ray system. Each filtered sample was dispersed on a TEM grid and placed in the SEM chamber. The sample was scanned with an electron beam energy of 20 kV and a beam current of approximately 1nA. Particles were recognized by the instrument as a set of contiguous picture elements with a backscattered electron (BSE) signal above an operator defined threshold. After particle recognition, the automated system remained on the particle and collected an EDX spectrum for identification of the elements present in the particle. Based on previous EDX analyses of colloid-coated filters, relative x-ray intensities were collected for the following elements: Na, Mg, Al, Fe, Si, P, S, Cl, K, Ca, and Ti. Compositional data was collected representing 500-1000 particle scan for each filtered sample.

TEM and SAED Analysis

For transmission electron microscopy (TEM), a small aliquot of the suspensions produced by each of the column experiments was evaporated on carbon thin films and analyzed on JEOL 2010 and 1200 electron microscopes equipped with a thin-window detector for EDX analysis of lighter elements ($Z > 6$). Selective area electron diffraction (SAED) patterns were used to identify the crystalline mineral phases with interplanar spacings calibrated using a sputtered gold standard.

Concentration and Thermal Analysis

To concentrate the dispersed sample for thermal analysis, the remaining suspensions generated from the column experiments were filtered through a 0.1 μm pore size polycarbonate filter. After the filtration was complete, the filter was placed in a

250 mL nalgene bottle that was filled to half its volume with DI water. The bottle containing the sample was then sonicated for 5 minutes to redisperse the concentrated suspension. Following sonication, the relatively clean filter was removed from the bottle and the remaining suspension was quick frozen with liquid N₂ and freeze dried to concentrate the particulate solids. Approximately 10 mg of freeze dried clay was placed in a platinum pan and heated from 50 to 800 °C at 20°C/min (TGA 2950, TA Instruments) using the dynamic rate high resolution mode (Res. 5). To improve thermal resolution, the heating rate is varied within a specified maximum and minimum, but is never reduced to zero (isothermal).

RESULTS

The texture and mineralogy of the samples used in the column studies (Table 1) were consistent with that observed in numerous deep cores of the water table aquifer underlying the Savannah River Site seepage basins. The clay mineralogy of both samples consisted primarily of kaolinite, goethite, and mica (Fig. 1), but the two materials differed appreciably in Fe oxide content, with the sample A and sample B consisting of 0.73 and 3.59 g Fe 100 gm⁻¹ respectively.

Table 1. Physical and chemical characteristics of the samples used in the column experiments.

Particle Size Distribution ^a	Sample	
	A	B
sand (>50 μm)	94.9	87.2
silt (50-2 μm)	0.8	4.5
clay (<2 μm)	4.3	8.3
pH		
pH _{water}	5.37	5.19
pH _{KCl}	4.4	5.03
EC ($\mu\text{S}/\text{cm}$)	5.86	8.57
Fe Oxides		
	Fe (g/100gm sample)	
CDB	0.73	3.59
AO ^b	0.006	0.017

^aMiller and Miller Method

^bMehra and Jackson Method (1960)

Column Results

For sample A, no significant effluent turbidity was observed in columns leached only with DI water, indicating that colloid generation was not an artifact of the disruptive influence of sampling and column packing. As reported by Seaman et al. (Chapter II) for samples from the same formation, turbidity increased only during the leaching of CaCl_2 solutions and the increase in turbidity coincided with a decrease in effluent solution pH (Fig. 2a). After the treatment solution was replaced with DI water, a second pulse in effluent turbidity was observed that decreased as the effluent pH began to rise and Ca was leached from the column (Fig. 2b). Because the cation exchange complex of these sediments was highly Al saturated, Seaman et al. (Chapter II) asserted that the decrease in pH that accompanied dispersion was the result of Al hydrolysis reactions and specific cation adsorption reactions, both of which would lower the solution pH and

increase surface positive charge on the matrix and the mobile colloidal phase. In contrast, the NaCl solution treatment was ineffective at lowering the effluent pH and generating a turbid suspension during leaching or when replaced by DI water. This was a reflection of the poor exchangeability of dilute Na solutions for Al held on the exchange complex of the column matrix (Nye et al., 1961). Consistent with the mechanism described by Seaman et al. (Chapter II), the positive electrophoretic mobility of the mobile colloids increased with decreasing pH as CaCl_2 was leached through the columns. When the treatment solution was replaced with DI water, the electrophoretic mobility decreased as the pH increased and the CaCl_2 solution was leached from the column.

Sample B, the sample with the highest Fe oxide content, initially produced a highly turbid suspension that decreased in concentration as the column was leached with the both treatment solutions (Fig. 3a). In contrast to conventional soil dispersion behavior, the initial suspension was more concentrated and remained more highly elevated (> 15 NTU) throughout the CaCl_2 treatment. Initially, the NaCl solution resulted in a less turbid suspension and the turbidity decreased faster and to a lower level than in the CaCl_2 treatments. Even when the treatment solutions were replaced by DI water, the CaCl_2 solution resulted in the higher effluent turbidity that remained elevated for a longer period of time than for the NaCl treatment. As observed for the low Fe oxide sample (Sample A), the effluent pH for the CaCl_2 treatment solution was lower than that observed for the Na treatment solution until the solution was replaced with DI water (Fig. 3b). In contrast to the low oxide sample (A), the effluent pH at which the colloid suspension was generated was higher for the high Fe oxide sample (B). Colloids generated from both treatment solutions displayed a positive electrophoretic mobility.

When at the Zero Point of Net Charge (ZPNC), clay suspensions will tend to flocculate regardless of the sodium adsorption ratio (SAR) or the background electrolyte concentration (Sposito, 1984). For samples that were lower in Fe oxides and higher in kaolinite (sample A), the decrease in pH was necessary to increase the positive charge developed on the exposed matrix until charge reversal occurred and the system fell below the ZPNC for the mineral assemblage. Even though a shift in solution composition was not required for dispersion to be observed in sample B, the positive

electrophoretic mobility of the resulting colloids and the influence of the solution cations on the extent and duration of the dispersion support the proposed mechanism, and indicate that the pH threshold and duration for dispersion of the positively charged suspensions are a function of the solution chemistry and clay mineralogy. The influence of the two cations on colloid transport and the resulting effluent solution pH reflect differences in Fe oxide and kaolinite content of the two samples. Seaman et al. (Chapter II) attributed the increase in dispersion from the leaching of divalent cation salts to an increase in the surface positive charge of the mobile colloidal Fe oxides and the exposed column matrix.

For both samples, non-disruptive sample drying was enough to inhibit the formation of a turbid suspension during the leaching of the treatment solutions or when the solutions were replaced with DI water (Fig. 2 and 3) and may explain why this type of dispersion behavior hasn't been widely observed. The ZPC of synthetic Fe oxides has been found to be somewhat sensitive to sample drying (Parks, 1967; Van Schuylenborgh, 1950). In a companion study, Seaman et al., (Chapter V) observed that drying reduced the degree of anion retardation expressed in tracer breakthrough experiments for the same highly weathered sediments.

Conventional SEM Results

In developing a flow chart for the identification of clay size minerals based on EDX spectra, Murdoch et al. (1977) admitted that it was often difficult to distinguish submicron particles based on morphology. To avoid these problems, EDX spectra of three reference materials are included for comparison with the spectra representing mobile colloids (Fig. 4). As expected, reference kaolinite consisted only of peaks representative of Al and Si in roughly equivalent concentrations (Fig. 4a) and the synthetic goethite with 0% Al substitution yielded peaks exclusively associated with Fe (Fig. 4b). Al-substitution in the goethite resulted morphologically in smaller, shorter crystal needles that displayed the associated Al peak in the EDX spectra (Fig. 4c).

Approximately 95% of the EDX patterns (200 spectra total) for the colloids generated in the column experiments could be unambiguously placed into one of five general mineral categories (Fig. 5): a) an Fe rich phase that contained varying amounts

of Al; b) an Al rich phosphate phase; c) a phase that contained approximately equal amounts of Al and Si attributed to kaolinite; d) a Ti rich phase; e) a Si rich phase; and f) an aluminosilicate phase that contained detectable levels of K attributed to mica. The remaining 5% percent of the patterns displayed compositional peak intensities that were intermediate between the five primary categories. The Fe rich phase was by far the most commonly observed pattern for both samples used in the column experiments (Table 2). Approximately 78 % of the EDX spectra for particles produced in sample A and 65% of those derived from sample B could be placed into the high Fe category. To varying degrees, all of the Fe rich spectra displayed a peak associated with Al. However, a shift in the X-ray diffraction patterns observed for the bulk clay of the two materials and the electron diffraction pattern of the mobile phase confirmed a high degree of Al substitution for Fe present as goethite.

Table 2. Particle categories observed using conventional SEM techniques.

EDXA Categories	Sample A (%)	Sample B (%)
Fe Oxide	77.86	65.00
Al-Phosphate	1.43	16.67
Kaolinite (1:1) Si/Al	9.29	5.00
Ti-rich	1.43	1.67
Si-rich (quartz)	1.43	3.33
Mica (2:1) Si/Al	3.57	1.67
Other	5.00	6.67
Total	100	1.00

As indicated by the five primary categories, the spatial resolution of SEM/EDX can provide information on the chemical composition of individual particles or small aggregates of particles rather than the bulk composition that would be determined by complete dissolution. A problem with this approach is that carbon sample coating necessary to perform SEM/EDX analysis limits the visual and photomicrographic resolution capability, making it difficult to distinguish primary particles and aggregates; conversely, Au-Pd coating enhances the visual resolution of SEM, but makes the

sample inappropriate for elemental EDX analysis. Elements representing multiple discrete solid phases may be incorrectly identified as one phase. For example, peaks associated with Fe were also commonly observed on the spectra for the other categories and most likely reflect Fe oxides aggregated to the surfaces of other particles.

Additionally, the limited resolving power of SEM, especially the more common thermionic emission source instruments, may also bias the identification of particles to larger size colloids that may not represent the most highly reactive surface area available for contaminant adsorption. The high degree of beam penetration into carbon-coated submicron-sized particles in SEM diminishes the quality of the image that is observed at the visual or television scan speed. This can result in particles that are almost invisible to the instrument operator during EDX analysis, but are sufficiently resolved under Au-Pd coating and the lower scanning speeds necessary to produce photomicrographs or digital images (Goldstein et al., 1992). To a degree, the limitations of SEM/EDX are illustrated in the identification and presentation of photomicrographs representing relatively large "mobile" ($> 1\text{-}2\text{ }\mu\text{m}$) particles by Ryan and Gschwend (1990) and Newman (1990).

With the exception of the quartz spectra (Fig. 5E), significant amounts of Fe were commonly detected on the other spectra and most likely reflect the limited resolving power of SEM/EDX, as smaller Fe oxide particles were observed to coat the polycarbonate filter and the surfaces of larger particles. Additionally, the large particle size observed for the quartz grains ($> 1\mu\text{m}$), also expressed in the low EDX background, indicates that the few quartz particles may actually reflect contamination of the filter with sand grains. Kaplan et al. (1994) also noted that high amounts of Fe in most of the EDX spectra for colloids within the contaminant plume. In general, the high EDX background often observed for the Fe-rich particles is a reflection of the limited resolution capability of SEM (large probe size) and the small particle size associated with these minerals. Under the higher resolution of Au/Pd coating, a dispersed coating of the smaller particles and aggregates was observed to dominate the filter surfaces of both samples. Representative SEM photomicrographs of the predominant particle morphology are included in Fig. 6. Larger particles displaying a platy morphology characteristic of layer

silicates, probably kaolinite, were also present but far less frequent and appeared to be coated or aggregated with a large number of the smaller rod-shaped particles.

With the exception of the Al-rich phosphate phase, the EDX categories defined in the present study were consistent with the mobile colloids observed within a subsurface contaminant plume (Kaplan et al., 1994). The Al-phosphate particles were far more common in the mobile colloids generated from sample B and may reflect the lower kaolinite content of that sample. For both samples used in the column experiments, the Al-phosphate phase consisted of particles that were approximately 200 to 500 nm in diameter and appeared to be associated with several of the smaller Fe rich particles. EDX analysis confirmed the presence of both Ca and Ba and suggests that these minerals represent a solid solution from the ideal structure of crandallite ($\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$) to gorceixite ($\text{BaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$).

Automated SEM Results

Several particle types were recognized in the sample (Table 3): Al-substituted Fe oxides were extremely common in both samples. Kaolinite was the most common phyllosilicate clay mineral observed and was usually coated with the Fe oxides. Aluminum phosphates and titania were present in trace level for both samples.

Table 3. Particle categories observed in automated SEM analysis.

EDXA Categories	Sample A (%)	Sample B (%)
Pure Kaolinite	1.98	1.98
Kaolinite + Fe	6.53	24.27
Al-sub goethite	63.09	48.03
Al-rich Phosphate	9.72	9.28
Ti-rich	0.50	0.48
Fe oxide + clay	18.17	15.70

TEM Results

TEM/EDX analysis confirmed the general compositional categories established by SEM/EDX analysis and indicated that the high Fe content found in most of the

SEM/EDX spectra was most likely associated with Fe oxides aggregated to the surfaces of other minerals. As observed in the SEM analysis of both column samples, the most common TEM/EDX patterns were associated with an Fe oxide and a Al-phosphate rich phase (Fig. 7). Numerous TEM photomicrographs and selective area electron diffraction patterns (SAED) indicated that goethite was the predominant crystalline Fe-oxide phase generated in the column experiments, but the presence of a fine grained less-crystalline Fe oxide phase in association with the mobile colloids cannot be ruled out (Fig. 8b). The presence of Fe oxides on the surface of the crandallite and other clay minerals was also indicated by the ring diffraction patterns of goethite superimposed on the single-crystal diffraction spot pattern (Fig. 9b) and an O to Al ratio that was greater than the value associated with the ideal structure of crandallite (Fig 7b). TEM/EDX analysis of the mobile colloids also revealed the presence of Sr in the Al phosphate indicating that the solid solution also approaches the Sr endmember, goyazite. TEM/EDX results also indicated that the Ti-rich Fe EDX spectra observed in the SEM probably resulted from the aggregation of a Ti oxide with the smaller Fe oxides (not shown).

Thermal Analysis

Thermal peaks associated with goethite and kaolinite were observed for the bulk clay fraction from each of the samples used in the present study (Fig. 10A). Crandallite was believed to be responsible for the hump ($\approx 400\text{--}450^\circ\text{C}$) observed on the kaolinite peak (Blanchard, 1971). With CDB treatment for removal of the free Fe oxides, the weight loss associated with crandallite became more evident (Fig. 10B). For the mobile colloids, the primary peak was that associated with the Fe oxides (CDB-extractable) and not the dominant clay mineral of the bulk samples, kaolinite. The thermal dehydroxilation observed for the mobile colloids and the bulk clay was somewhat lower than that normally reported in the literature for goethite and was most likely a reflection of the high degree of Al substitution present in the goethite.

DISCUSSION

The significance of colloid transport in facilitating the movement of adsorbing contaminants depends not only on the concentration and mobility of the solid phase, but also the affinity of the contaminant for the surface of the mobile solid phase. Reynolds and Gschwend (1987) pointed out that although smaller mobile particles (<100nm) collected from an aquifer may be present in higher numbers, their combined mass may still be less than that of a few relatively large particles (>600nm). Although this overlooks the importance of mineralogy and surface area in controlling contaminant adsorption processes, the mass contribution of a few select large particles can have a great impact on the bulk elemental composition of the suspension. For example, the total mass of a few relatively large and unreactive quartz grains as observed in the present study or a few large clay platelets can significantly influence the composition of the suspension derived from total dissolution. Additionally, the reliance on SEM/EDX as the sole non-destructive identification and characterization technique may neglect small, high surface area minerals, resulting in the incorrect identification of the mobile solid phase actually responsible for contaminant transport.

In soils and geologic formations, Fe and Al oxides are often considered cementing or coagulating agents because they possess a net positive charge under many environmentally relevant conditions, and their presence has been shown to stabilize clay systems against the dispersive effect of high exchangeable sodium levels (Shainberg et al., 1987; Goldberg and Glaubig, 1987; Schwertmann and Taylor, 1989). Because of the low ZPC of quartz ($\text{pH} \approx 2.0$) and the presence clay minerals that carry a permanent negative charge, most groundwater matrices are viewed as having a negative charge that would tend to electrostatically limit the mobility of colloidal solids at pH values below their ZPC. Therefore, column experiments are often biased towards factors that enhance the movement of negatively charged colloids through a negatively charged matrix. When Fe and Al oxides have been reported to be extensively mobile, they usually possess a net negative charge resulting from the surface adsorption of organics (Liang et al., 1993; Ryan and Gschwend, 1990; Kaplan et al., 1993).

Even at pH values below their PZC where the surface displays a net positive charge, Fe and Al oxides retain a high affinity for polyvalent cations, especially alkaline

earth and transition metals (Kinniburgh et al., 1975; Kinniburgh et al., 1976). The specific adsorption of polyvalent cations has been shown to increase the surface positive charge of Fe oxides, but the significance of this mechanism in the field has not been well documented (Bleam and McBride, 1984; Uehara and Gillman, 1981). For a negatively charged matrix, the adsorption of polyvalent cations would tend to enhance flocculation/filtration by compressing the repulsive diffuse double layers in agreement with the Schulze-Hardy rule; thus, limiting the importance of colloid transport of these species at anything greater than trace concentrations. In contrast, the specific adsorption of these species onto oxide surfaces under moderately low pH conditions would tend to enhance the mobility of the phase through a matrix whose surface character is dominated by hydrous oxides. Additionally, the high-valent cation may actually shield any negatively charged sites present on the mobile colloids or the immobile matrix and reduce the coulombic attraction between surfaces with opposite charges.

The existence of a positively charged mobile colloidal phase is most often associated with extremely acidic conditions (Kaplan, 1993), but the results of this study clearly indicate that mild changes in groundwater composition associated with contamination or even certain reclamation practices can result in the formation of a dilute stable Fe oxide suspension without requiring dramatic changes in pH or redox potential. Even at pH values below their ZPC, Fe and Al oxides can retain a high affinity for polyvalent cations, especially alkaline earth and transition metals (Kinniburgh et al., 1975; Kinniburgh et al., 1976). Using synchrotron x-ray fluorescence, Kaplan et al. (1994) observed that seepage basin contaminants (Cr, Ni, Cu, and Pb) were associated with an Fe rich phase that displayed a positive electrophoretic mobility. The reduced occurrence of this phase in the vicinity of the seepage basin may reflect the enhanced mobility and preferential transport of the Fe oxides with the initial breakthrough of the contaminant plume. Additionally, the present results indicate that the sensitivity (ie. dispersibility) of a geologic formation to changes in solution composition can vary dramatically within materials of similar texture, mineralogy, and origin. In addition to increasing the mobility of sparingly soluble contaminants, the mobile colloidal phase is likely to increase the concentration of native metals detected in acidified or unfiltered

groundwater samples.

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Figure 1. X-ray diffraction pattern of the clay fractions (Mg-saturated) from the two samples used in the column experiments.

Figure 2. The influence of treatment solution (0.001 N CaCl_2 or NaCl) and sample drying on effluent turbidity (A), pH (B), and electrophoretic mobility of mobile colloids from sample A. Columns were leached with a given treatment solution for 10 pore volumes followed by several pore volumes of DI water (*160 EDXA spectra

Figure 3. The influence of treatment solution (0.001 N CaCl_2 or NaCl) and sample drying on effluent turbidity (A), pH (B), and electrophoretic mobility of mobile colloids from sample B. Columns were leached with a given treatment solution for 10 pore volumes

Figure 4. EDX spectra of known minerals for comparison with colloids collected in column experiments: a) kaolinite (KGa-2); b) synthetic Al-free goethite (Schwertmann and Cornell, 1991 pg. 64); c) synthetic Al-sub. goethite ($\approx 10\text{-}12\%$ Al sub., Schwertmann and Cornell, 1991 pg. 71).

Figure 5. General colloid categories as derived from SEM/EDX analysis: a) Fe/Al rich phase; b) Al/P rich phase; c) Si:Al, 1:1 (kaolinite); d) Ti rich Fe oxide; e) Si rich phase (quartz); and f) Si:Al, 2:1 phase with detectable K.

Figure 5. Continued.

Figure 6. Typical scanning electron micrograph of Au-Pd coated particles deposited on 0.10 μ m pore size polycarbonate filter.

Figure. 7. TEM/thin window EDX spectra of Fe rich and Al/P phases identified in SEM.

Figure 8. Transmission electron micrograph (A) and selective-area diffraction patterns (B) of fine-grained goethite.

Figure 9. Transmission electron micrograph (TEM) of crandallite with surface coating of fine-grained goethite (A). Selective-area diffraction pattern of crandallite with superimposed rings associated with goethite (B).

Figure. 10. Derivative weight loss as a function of temperature for the bulk clay from sample D (curve A), the bulk clay minus Fe oxides (curve B), and mobile colloids generated in column studies (curve C).

CHAPTER IV:

Ionic Tracer Movement Through Highly Weathered Sediments

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ABSTRACT

A highly-weathered, sandy aquifer material from the Upper Coastal Plain region of the Southeastern U.S.(Aiken, SC) was used to determine the impact of ionic strength and solution composition on the determination of physical transport parameters using ionic tracers. The mineralogy of the clay fraction consisted primarily of kaolinite, goethite, and mica. Repacked saturated columns (bulk density $\approx 1.5 \text{ g cm}^{-3}$) were leached at a constant rate ($\approx 0.25 \text{ cm min}^{-1}$) with a given tracer solution. For comparison, tritium ($\approx 200 \text{ pCi}$) was included in selected columns and several of the experiments were replicated in columns of acid-washed sand. Pore volume estimates based on tritium breakthrough were consistent with those calculated from the bulk density of the repacked matrix. In contrast, solute breakthrough for the sandy geologic material was dependent on concentration, as well as cation and anion type. At low ionic strengths ($0.0005\text{-}0.010M$) that are analogous to conditions that may be encountered in field-scale transport experiments, neither the cation nor the anion acted conservatively, yielding systematically high estimates of column porosity or low estimates of flow velocity. At the higher ionic strengths ($\approx 0.10M$), solute breakthrough was essentially conservative regardless of ionic composition. The impact of cation valence and concentration on Br^- breakthrough was determined using MgBr_2 and KBr solutions of varying concentrations ($0.001\text{-}0.1N$). Bromide breakthrough was substantially delayed for concentrations below $0.10 M$ and was delayed to a greater extent in the presence of a divalent cation (Mg) than in the presence of a monovalent cation (K). Failure to recognize these interactions in the field could lead to a false interpretation of Br displacement in terms of physical interactions, i.e flow velocity,

dispersivity, etc.

INTRODUCTION

Hydrologic modeling describes the transport of a nonreactive tracer as a function of mass flow (advection), based on the hydraulic conductivity (K) of the transmissive zone, and a combination of other factors such as diffusion and small-scale variations in flow path and velocity (hydrodynamic dispersion). Transport parameters, such as the pore water velocity ($V = L t^{-1}$) and dispersion coefficient ($D = L^2 t^{-1}$), are determined by calibration of the advection-dispersion equation to the spatial distribution or breakthrough of a "non-reactive" tracer (Parker and van Genuchten, 1984). An assumption is made that the position of the solute plume is a manifestation of the physical properties of the transmissive zone and not a function of chemical interaction between the tracer and the porous media.

The basic equation for the transport of an interactive tracer under steady-state water flow conditions in a one-dimensional homogeneous system is

$$\frac{\rho}{\theta} \frac{\partial S}{\partial t} + \frac{\partial C_r}{\partial t} = D \frac{\partial^2 C_r}{\partial x^2} - V \frac{\partial C_r}{\partial x} \quad [1]$$

where ρ is the bulk density of the porous media, θ is the volumetric water content, C is the concentration of the compound of interest in the liquid phase, S is the adsorbed concentration per unit mass of solid phase, x is the distance, and t is time. For simplicity of discussion, a linear equilibrium adsorption model,

$$S = k C_r \quad [2]$$

where k is an empirical partitioning constant, will be employed. Substituting the above adsorption term into the transport equation yields

$$R \frac{\partial C_r}{\partial t} = D \frac{\partial^2 C_r}{\partial x^2} - V \frac{\partial C_r}{\partial x} \quad [3]$$

where R , the dimensionless retardation factor, can be defined as

$$R = 1 + \frac{\rho k}{\theta} \quad [4]$$

Ideally, a non-reactive tracer ($R = 1$) allows the measurement of the transport parameters (V and D) without altering the fluid properties of the groundwater or the surface chemical and transmissive properties of the aquifer matrix. However, when chemical interactions are combined with the physical processes of transport, it becomes difficult to distinguish between a nonlinear adsorption process under the influence of a constant flow gradient, and a linear or pseudo-linear adsorption process under the influence of a more complicated flow regime.

Surface/solute interactions that alter surface charge on the clay mineral fraction can influence the transport of ionic solutes through subsurface systems. Clay minerals can be divided into two basic groups according to the origin of surface charge; (1) constant surface charge minerals and (2) constant surface potential or variable charge minerals. Most soils and geologic systems represent hybrids of the two basic groups because they are composed of varying quantities of both mineral types, and because the edges of constant charge clay minerals display variable charge character. The Zero Point of Net Charge (ZPNC) for a mixed system is the pH at which the anion exchange capacity and the cation exchange capacity are equivalent under a given set of solution conditions (Sposito, 1984).

For variable charge minerals, surface charge is created by the excess adsorption of the potential determining ions (H^+ and OH^-) at the mineral surface; thus, the sign and magnitude of surface charge can vary with the concentration and activity of these two species. The Zero Point of Charge (ZPC) for a constant potential mineral is the pH at which the total net particle charge vanishes under a given set of solution conditions (Sposito, 1984). Depending on mineral composition and the degree of crystallinity, the

ZPC for hydrous Fe and Al oxides is generally in the pH range of 7 to 9 (van Olphen, 1977). Under pH conditions below the ZPC, the mineral will possess a net positive charge; conversely, at pH values above the ZPC the surface will be negatively charged. In addition, the surface charge density of a variable charge mineral is a function of: i) valence of the counter ion, ii) dielectric constant of the solution, iii) temperature, iv) electrolyte concentration, v) pH of the bulk solution, and vi) the ZPC of the oxide mineral (Uehara and Gillman, 1981). Also, specific adsorption of polyvalent cations or anions at the oxide surface can alter the expression of net surface charge (Uehara and Gillman, 1981; Stumm and Morgan, 1981).

Under most field conditions bromide and chloride are characterized as "conservative" or "nonreactive" tracers (Freyberg, 1986; Jensen et al. 1993; Gelhar et al., 1992) due to the coarse texture of the groundwater matrix and the assumed presence of constant/negatively charged clay minerals. In many instances this may be a valid assumption. For example, chloride migrated at essentially the same rate ($V = 0.7 \text{ m d}^{-1}$) as tritium ($V = 0.75 \text{ m d}^{-1}$) in a sandy aquifer in Denmark, but a greater vertical spreading of the chloride plume was attributed to differences in density between the native groundwater and the more concentrated tracer solution (Jensen et al. 1993). However, the non-conservative ($R \neq 1$) movement of anionic tracers has been well documented in laboratory column studies (McMahon and Thomas, 1974; Ishiguro et al., 1992; Chan et al., 1980; Wong et al., 1990) and has been reported in some field experiments (Boggs and Adams, 1992). The most often recognized non-conservative interaction ($R < 1$) is anion exclusion, resulting in more rapid tracer movement than can be attributed to water flux (Thomas and Swoboda, 1970; Cameron and Wild, 1982). This interaction is so commonly acknowledged that the definition of a conservative tracer is often expanded to include tracers that move at a rate greater than water flow ($R < 1$).

Although exclusion and adsorption have an opposite effect on the transport

velocity of a given ionic species, both are controlled by the expression of surface charge and its neutralization at the solid/solution interface. McMahon and Thomas (1974) found that the degree of anion exclusion compared to tritium increased with increasing cation exchange capacity of the soil matrix. Thomas and Swoboda (1970) observed that the degree of exclusion in a clayey soil decreased with increasing concentration of the tracer, but they attributed the increase in effective pore volume to the enhanced ability of the anion to diffuse into the clay interlayers rather than a change in the interlayer spacing or physical associations of the clay constituents. In addition to tracer concentration, (McMahon and Thomas (1974) observed that the degree of anion exclusion or retardation can be altered by physical sample disruption that destroyed the natural soil structure or changed the spacial distribution of the clay minerals.

In contrast to anion exclusion, the delayed arrival of Br and Cl has been observed in soils and sediments that contain significant quantities of variable charge clay minerals (McMahon and Thomas, 1974; Ishiguro et al, 1992; Chan et al., 1980; Berg and Thomas, 1959; Boggs and Adams, 1982). For example, Chan et al. (1980) observed that Cl⁻ breakthrough in an oxidic soil was dependent on both the pH and ionic strength of the treatment solution. Ishiguro et al. (1992) noted that under fixed ionic strength conditions, Br⁻ was delayed to a greater extent in an allophanic andisol at low pH values (ca. 4.2), while Sr²⁺ was retarded to a greater extent at high pH values (ca. 7.7). Under intermediate pH conditions (5.6) and low solution concentrations (<0.01M), which are analogous to those usually experienced in the field, neither the cation nor the anion behaved conservatively. Because many factors influence surface charge development, the mobility of a solute through porous media containing variable charge minerals is highly dependent on the exact solution conditions. Such interactions are more clearly recognized by focussing on both ionic species being transported in a cation-anion pair (i.e. KBr, K₂SO₄, etc.).

The objective of this study was to determine the influence of surface chemical

interactions on the transport of ionic tracers in highly-weathered sediments and to illustrate the impact of these interactions on the derived transport parameters. Solute breakthrough experiments were conducted using a coarse-textured subsurface material representative of the highly weathered alluvial sediments common in the vadose zone and upper saturated zone of the Upper Coastal Plain of the southeastern US. Column studies focused on dilute tracer solutions representative of the low ionic strength pore waters and groundwaters native to these sediments.

MATERIALS AND METHODS

Sample Collection and Storage. Bulk material for the column study was collected on the Department of Energy's Savannah River Site which is located on the Aiken Plateau of the Upper Atlantic Coastal Plain. The vadose zone and the upper saturated zone consist mainly of red, fine to coarse sands, and clayey sands with interbeds of clay, sandy clay, and gravel. To avoid bentonite contamination and sample disruption caused by conventional drilling, field moist material was collected from a deep erosional exposure of sediments representative of the vadose and upper saturated zones. The pH and electrical conductivity (EC) of the sample were determined in 2:1 ratio (solution/sample) with DI water, and the particle-size distribution was determined by the micro-pipette method (Miller and Miller, 1987). Triplicate samples were stirred intermittently for 30 minutes prior to pH and EC measurement.

X-Ray Diffraction. The clay fraction was dispersed by saturation with Na_2CO_3 (pH 10) and then separated by centrifugation (Jackson, 1979). Aliquots of the clay suspension were plated on petrographic slides using the Drever method (1973), and analyzed by x-ray diffraction from 2 to $30^\circ 2\theta$ using Cu K α radiation and a Phillips Norelco diffractometer equipped with a graphite monochromator. Treatments consisted of Mg^{2+} , Mg-ethylene glycol (Mg-EG), and K^+ saturation, the latter of which was heat

treated at 110, 300 and 550 °C prior to x-ray analysis.

Exchangeable Cations. Exchangeable cations were extracted with 0.5 M BaCl₂, and the extracts were analyzed by atomic-absorption spectroscopy for Na⁺, Ca²⁺, Mg²⁺, K⁺, and Al³⁺. Cation exchange capacity (CEC) was estimated by summing the BaCl₂ extractable cations.

Column Experiments. The column experiments were performed in 10 cm long plexiglass tubes with an interior diameter of 5 cm (Fig 1). Field moist sample was packed in columns to a uniform density of $\approx 1.5 \text{ g cm}^{-3}$. Columns were oriented vertically and slowly saturated from the outlet with deionized water ($< 0.25 \text{ mL min}^{-1}$). After saturation, the columns were turned horizontally and flow was initiated with a given tracer solution at a constant Darcy Velocity of $\approx 3.6 \text{ m d}^{-1}$.

The influence of various solution factors on the transport velocity of ionic solutes was observed using several different solutions. Each repacked column was used to test the breakthrough of a single solution before the matrix was replaced with fresh material. The influence of concentration and ion valance on the transport histories (i.e. behavior) of various ionic solutes was observed using 0.001 to 0.1 *N* solutions made from various Na⁺, Ca²⁺, Cl⁻ and SO₄²⁻ salts. To demonstrate how these interactions can influence the transport velocity of a commonly used "conservative" anion (Br), columns were leached with 0.001 to 0.1 *N* tracer solutions derived from MgBr₂ or KBr. In addition to the single component solutions, the influence of pH and carrier anion on the movement of mixtures of Na⁺, Ca²⁺, and Mg²⁺ was observed for a complex mixture derived from Cl⁻ or SO₄²⁻ salts that had been pH-adjusted over a range of 5 to 10. Column effluents were analyzed by atomic-absorption spectroscopy (AAS) for Na⁺, Ca²⁺, Mg²⁺, K⁺, and Al³⁺. For comparison, tritium ($\approx 200 \text{ pCi/mL}$) was included in selected columns to calibrate the matrix pore volume. The electrical conductivity and pH of the effluent were monitored continuously, and leachate fractions were collected for cation,

bromide and tritium analysis.

Bromide Analysis

Effluent bromide concentrations were determined using a Br⁻ selective electrode (FK1502Br, Radiometer) attached to a PHM 84 Research pH meter (Radiometer Inc.) set to measure mV. The voltage output was calibrated using a 0.1 M NaBr standard diluted over four orders of magnitude. The ionic strength of the samples and standards was adjusted by the addition of NaNO₃ to ensure that the ionic strength of the samples differed by less than 10 %.

Tritium Analysis

Two mL of the effluent fractions were mixed with 10 mL of scintillation cocktail and counted for 20 minutes (Packard Instru. Co.). Due to the low concentration of tritium in the tracer solution, effluent tracer concentrations were calibrated to various known dilutions of the inlet tracer solution.

Breakthrough Analysis

Effluent tracer concentrations were plotted as maximum dimensionless concentration (C/C_0) where C_0 was the input concentration. Transport parameters V , D and R were estimated using the least-square inversion method (CXTFIT) of Parker and van Genuchten (1984). Model 2, a deterministic linear equilibrium adsorption model consisting of one region, was calibrated to the effluent concentration data. The lack of extensive tailing for the breakthrough and leachout of tritium indicated that a one-region model was sufficient to describe the narrow distribution of flow velocities within these coarse-textured materials. Two possible cases were evaluated for each set of breakthrough curves: a) the retardation factor (R) for the solute of interest was assumed to be 1 (no interaction) and the pore water velocity was estimated by the model, and b)

the pore water velocity ($V=q/q$) was estimated from the inlet flux and the volumetric water content of the column, and R was estimated by the model. In both cases the model was allowed to estimate D . Because two adjustable parameters were fitted in each case, the resulting r^2 and predicted breakthrough curve (BTC) were identical. The volumetric water content (q) was assumed to be equivalent to the column porosity because of the coarse texture of the column matrix. Assuming a particle density (ρ_p) of 2.65 Mg m^{-3} , the total column porosity was estimated from the bulk density (ρ_b) and total volume for each repacked column (Danielson and Sutherland, 1986).

RESULTS AND DISCUSSION

Sample Characteristics

The particle size distribution of the sandy subsurface material was consistent with that observed throughout the upper saturated zone ($< 10\%$ clay) with very little silt present. The clay fraction, as determined by x-ray diffraction, consisted primarily of kaolinite, goethite, and mica (illite) while the coarse fraction ($>2\mu\text{m}$) was almost exclusively quartz. The cation exchange capacity (CEC) of the bulk material, estimated from the total sum of Ba^{2+} extractable cations, was extremely low ($0.625 \text{ cmol}(+) \text{ kg}^{-1}$), with a major portion of the exchange complex occupied by exchangeable Al ($\approx 85\%$) (Table 1).

Table 1. Physical and chemical characteristics of sample used in column experiments.

cation	cmol ₍₊₎ kg ⁻¹ x 10 ³	SD ^b x 10 ³
Na	2.4	0.4
Ca	14.7	1.2
Mg	72.1	6.7
K	5.8	0.6
Al	530	63
CEC ^c	625	72
ESP ^d	0.38	0.03
ex. Al %	84.8	0.037
	g 100 g ⁻¹	SD ^b
Sand	90.6	1.3
Silt	1.3	1.3
Clay	8.2	2.0
Sand Fractionation		
>1mm	7.9	
>500μm	24.5	
>250μm	27.5	
>106μm	40.5	
>53μm		
<53μm		
1:2 soil to solution ratio		
pH _{water}	4.94	0.04
pH _{KCl}	4.42	0.07
EC _{μS/cm}	5.47	0.49

^aExtractable in 1N BaCl₂^bStandar Deviation^cSum of Extractable Cations^dExtractable Na Percentage

Breakthrough 0.001 N Salts (Fig. 2A)

Initially, EC was used as an estimate of breakthrough for the various salt solutions. Though EC is insensitive to ionic identity, it represents the most conservative estimate of the possible inlet solute breakthrough under conditions where the tracer solution was significantly higher in ionic solutes than the initial pore water (i.e., $1 \leq R_{EC} \leq R_{inlet\ solutes}$). If solute transport was occurring by piston flow, the leaching front of a conservative tracer should show an immediate breakthrough that coincides with one pore volume. Tritium breakthrough was consistent with pore volume estimates based on the column bulk density (Fig. 2A). However, the obvious delay of ionic solutes with respect to the breakthrough of tritium confirms that both treatment solution cations and anions were retarded, and the degree of retardation was dependent on the identity of the treatment solution cation and anion, indicating that both the apparent anion and cation exchange capacity were sensitive to solution conditions. If simple equivalent exchange was occurring within the column, native cations and anions should be released into solution in equivalent concentrations to those retained; thus, the breakthrough of EC would still coincide with that of tritium, even though the actual composition of the solution may have changed dramatically. Of the 0.001 *N* solutions tested, NaCl yielded the most conservative breakthrough, but was still significantly retarded compared to tritium. Calcium chloride eluted next, followed by Na₂SO₄, and finally CaSO₄. If the 0.001 *N* solutes were considered to be conservative ($R=1$), at least in terms of equivalent exchange, the volumetric water content estimated by CXTFIT (Table 2) ranged from 0.64 to the physically unrealistic value of 2.66, dramatically different from the values based on bulk density or tritium breakthrough.

Table 2. Column transport parameters estimated with Model 2 of CXTFIT (Parker and van Genuchten, 1984).

					CXTFIT	EST	
	Est. V ^a	CXTFIT V ^a	D ^b	R ^c	θ	θ	r ²
0.001 N salt breakthrough (Fig. 2)							
NaCl	0.59	0.40	0.15	-	0.64	0.43	1.00
	0.59	-	0.22	1.44	-	0.43	1.00
CaCl ₂	0.59	0.31	0.18	-	0.83	0.43	1.00
	0.59	-	0.36	1.92	-	0.43	1.00
Na ₂ SO ₄	0.59	0.23	0.21	-	1.09	0.43	1.00
	0.59	-	0.53	2.55	-	0.43	1.00
CaSO ₄	0.60	0.10	0.08	-	2.66	0.43	0.99
	0.60	-	0.53	5.75	-	0.43	0.99
0.1 N salt breakthrough (Fig. 3)							
NaCl	0.60	0.58	0.25	-	0.44	0.43	1.00
	0.60	-	0.25	1.03	-	0.43	1.00
CaCl ₂	0.60	0.58	0.09	-	0.44	0.43	1.00
	0.60	-	0.10	1.04	-	0.43	1.00
Na ₂ SO ₄	0.60	0.54	0.13	-	0.47	0.42	0.95
	0.60	-	0.14	1.12	-	0.42	0.95

Table 2. Continued.

Influence of Ionic Strength on Br breakthrough							
0.001	0.60	0.29	0.13	-	0.89	0.42	0.99
	0.60	-	0.28	2.10	-	0.42	0.99
0.01	0.60	0.45	0.23	-	0.56	0.42	1.00
	0.60	-	0.30	1.31	-	0.42	1.00
0.1	0.63	0.56	0.27	-	0.45	0.41	1.00
	0.63	-	0.30	1.16	-	0.41	1.00

^aPore water velocity (cm/min)^bHydrodynamic dispersion coefficient (cm²/min)^cRetardation Factor

Even though the Al concentration in the column effluent was below the detection limit for flame AAS, the degree of retardation observed for the various salt solutions and the effluent pH trends suggest that exchangeable Al was playing a major role in buffering the pH of the system and in controlling the solute migration behavior. Exchangeable aluminum combined with oxide surfaces can act as "apparently" nonequivalent sinks for both solution cations and anions.

After exchange with treatment solution cations, aluminum hydrolysis reactions reduce the equivalency of the exchanged Al species and generate acidity that buffers the pH in favor of continued anion sorption. However, readsorption of Al hydrolysis products, especially on kaolinite (Hodges and Zelazny, 1983), make it difficult to perform charge and mass balance estimates based on the composition of column effluents (Seaman et al., 1995; Parker et al., 1979).

In the absence of a source of acidity (reaction 5), net adsorption of anions on variable-charge oxide surfaces should result in a shift in pH towards the ZPC of the sorbing mineral (Uehara and Gillman, 1981). Therefore, anion adsorption by variable-charge surfaces in the column system consumes acidity generated by Al-exchange and hydrolysis, and the coupling of these two reactions between the different surfaces results in a greater net-cation and anion adsorption than would be occur by either reaction alone.

Despite the obvious differences in retardation, NaCl and CaSO₄ solutions resulted in approximately the same effluent pH histories (Fig. 2B), which changed little during the course of leaching and reflected similar preferences of the two reactions for both cation/anion pairs (Uehara and Gillman, 1981). For the NaCl solution, neither ion was capable of displacing surface forms of acidity or alkalinity and the solution pH remained essentially unchanged. In the case of the CaSO₄ solution, the two ions were approximately equal in their ability to displace surface acidity and alkalinity; exchangeable Al³⁺ and protons in the case of Ca²⁺ and surface hydroxyls in the case of SO₄²⁻. The presence of SO₄²⁻, an anion with a higher affinity for the oxide surface than Cl⁻, tends to increase solution pH by displacing hydroxyls from oxyhydroxide surfaces (Hohl et al., 1980), which neutralizes aluminum or surface protons exchanged by Ca²⁺. In the case of the Na₂SO₄ solution, SO₄²⁻ was effective at displacing surface hydroxyls, whereas the Na⁺ was unable to effectively displace Al³⁺, thus increasing effluent pH (Nye et al., 1961).

Breakthrough of 0.100 N Salts

When the equivalent concentration of the treatment solutions was raised to 0.1 N

, the identity of the cation and anion had little influence on the EC breakthrough (Fig. 3A) and the two estimates of q were fairly consistent (Table 2). In other words, at the point when the anion begins to act conservatively the entire solution, in terms of net equivalents, functions conservatively with respect to EC breakthrough. To some degree this is a function of the coarse texture of the matrix and the requirement for maintaining electrical neutrality within the column, but it illustrates that any solute can be used as a conservative tracer if its concentration greatly exceeds the adsorption capacity of the matrix. It is important to note that even the $0.001N$ solutions are several times more concentrated than native groundwater of this region (Strom and Kaback, 1992).

As observed at the lower ionic strengths, the effluent pH results from a balance between anion adsorption on the oxide surface that tends to increase the pH, and cation exchange and Al hydrolysis that tends to lower the pH. When the anion adsorption capacity of the matrix was exceeded at the higher concentrations, the effluent pH was dominated by the reactions of Al exchange and hydrolysis; thus, a decrease in pH was observed regardless of cation or anion valence. However, the relative order with respect to effluent pH was consistent with the ability of the treatment cation to replace exchangeable Al and the sorption preferences for the treatment anions that were observed at lower ionic strengths.

Influence of Anions on Cation Selectivity

Mixed cation solutions ($250 \text{ mg L}^{-1} \text{ Na}$, $15 \text{ mg L}^{-1} \text{ Mg}$, $5 \text{ mg L}^{-1} \text{ Ca}$) prepared from either sulfate or chloride salts were pH-adjusted over the range of 5.6 to 10.0 prior to conducting leaching experiments (Fig. 4). Transport of these mixed cation solutions illustrates the sensitivity of this system to mild changes in solute composition. At the high inlet concentration, sodium displayed the most conservative transport behavior of the three cations, but was delayed to a greater extent in the presence of sulfate and with increasing pH (Fig. 4B). The impact of solution pH and anion valence was even more

dramatic for the transport of divalent solution cations, Ca^{2+} and Mg^{2+} . In the presence of chloride, Mg^{2+} was concentrated in the initial effluent due to competition with Ca^{2+} for exchange sites and the release of native Mg^{2+} from the exchange complex (Fig. 4A). This was much less evident at the higher pH regimes and Mg^{2+} became only slightly elevated compared to the inlet concentration. With prolonged leaching of the high pH solution, the effluent Mg concentration actually decreased to about half of that of the inlet solution, reflecting an increase in Mg adsorption and the "effective" cation exchange capacity of the column matrix when leached with the alkaline treatment solution, even though the effluent pH was the same as the pH 5.6 solution treatment. Calcium displayed the highest degree of retardation that increased with increasing inlet pH.

When the inlet solutions were comprised of sulfate salts, the breakthrough of Mg^{2+} and Ca^{2+} was dramatically different from that of chloride salts (Fig. 4B). The transport of Mg^{2+} was retarded to a greater extent, and the concentration failed to surpass the inlet concentration until ≈ 6 pore volumes had been passed through the column. At the higher pH, the Mg^{2+} concentration was never higher than the inlet concentration during the first 10 pore volumes of leaching. Calcium was delayed to a greater extent in the presence of sulfate and the degree of retardation increased at higher influent pH values.

The effluent pH of the column was more dependent on the treatment anion than on the pH of the inlet solution, illustrating the influence of the anion on surface chemical reactions controlling the buffering capacity of the aquifer sediments (Fig. 4C). The same approximate effluent pH was observed regardless of the influent pH of a given anion treatment. The decrease in pH observed for the chloride solutions was not observed for the sulfate treatments because of the greater ability of the sulfate ligand to exchange for surface hydroxyls present on the variable charge surfaces, thus buffering the solution against acidity generated either by specific adsorption of treatment cations or Al

exchange and hydrolysis (Alva et al., 1991). Even though the same effluent pH was observed for all solutions derived from a given anion, the higher pH inlet solutions appear to be effective at generating cation exchange capacity within the column through a combination of increasing the net-negative charge on oxides and neutralizing exchangeable Al. The effluent solution pH for the sulfate treatment approached that of the chloride solution with continued leaching and may reflect a limit to the ability of the sulfate interaction with the oxide surface to counter any downward shift in pH caused by Al hydrolysis.

The increase in retardation of treatment cations in the presence of sulfate has been attributed to the increase in pH and surface negative charge that accompanies sulfate adsorption on variable charge minerals such as Fe oxides (Bolan et al., 1993). Wann and Uehara (1980) observed that the affinity of an oxidic soil for Ca^{2+} and Mg^{2+} increased with increasing levels of applied phosphate. In addition to these mechanisms, coadsorption of the cation and anion has been suggested to increase cation retention for oxisols in the presence of sulfate (Alva et al., 1991; Marciano-Martinez and McBride, 1989).

Br Breakthrough

The influence of solution composition on the breakthrough of ionic species was also illustrated in the retardation of Br^- . Estimates of pore volume based on tritium breakthrough were consistent with those based on bulk density and typically differed by less than 5 %. At higher concentrations (1.0-0.1M), the breakthrough was essentially unaffected by Br^- concentration and the valence of the carrier cation (Fig 5). At concentrations below 0.1 M, breakthrough was dependent on both the concentration of the tracer solution and the valence of the carrier cation. Retardation factors for Br^- ranged from a low of 1.16 for 0.1 N KBr to 2.10 for 0.001N KBr; however, the low ionic strength solutions of MgBr_2 displayed the greatest delay in breakthrough. The

increased retardation of Br^- in the presence of Mg^{2+} may be due in part to the adsorption of the polyvalent cation to the oxide surfaces at pH values below the oxide ZPC (Kinniburgh et al., 1975) resulting in a decrease in solution pH and an increase in net positive surface charge (Bleam and McBride, 1984). In addition, the greater ability of Mg^{2+} compared to K^+ to exchange with Al^{3+} would tend to lower the solution pH and thus increase the net-positive charge on the Fe oxide surface. Although the BTCs differ in shape for the two acid washed sand columns (Fig. 5B), Br^- derived estimates of porosity were independent of ionic strength or carrier cation (not shown) and consistent with those based on the bulk density of the column matrix.

The influence of ionic strength and counter ion valance on anion retardation can be explained by the Gouy-Chapman diffuse double layer model of surface charge. Under conditions of constant pH, the surface charge of a variable charge mineral is proportional to the square root of the concentration of an indifferent electrolyte, in this case the tracer solution (Uehara and Gillman, 1981). Even though this predicts that the number of anion adsorption sites for a mineral below its ZPC will increase with increasing concentration of the tracer, the total percentage of the inlet solution anions adsorbed for a given ionic strength decreases dramatically as the concentration is increased. Regardless of the proposed mechanism of ion retardation, the adsorbed ion will approach conservative behavior as its concentration exceeds the adsorption capacity of the matrix and the ability to experimentally detect minute degrees of retardation; conversely, retardation will increase dramatically if the inlet concentration is low relative to the sorption capacity of the matrix.

CONCLUSIONS

The simultaneous retardation of both cations and anions without an obvious exchange for native ionic species suggests not only a heterogeneity with respect to surface charge and adsorption sites, but also an adsorption mechanism that would tend

to generate roughly equivalent cation and anion sites within the aquifer matrix. This surface/solute interaction often referred to as "salt sorption" has been widely observed in batch adsorption studies of highly weathered soils, but it may not be easily recognized in solute transport experiments because of the tendency to focus on the fate of a particular cation or anion and neglect the influence or fate of the counter ion.

Several possible mechanisms can be invoked to account for the simultaneous retardation of both cations and anions without an obvious exchange for native species, but experimentally distinguishing between these mechanisms or combinations of these mechanisms based on bulk solution data in complex systems containing several types of surfaces may be difficult, if not impossible. Anion retardation is usually attributed to adsorption on the Fe and Al oxide fraction, but the simple model of adsorption on a single variable charge surface such as goethite, was inadequate to describe the observed shifts in effluent pH and both cation and anion transport behavior. Wada (1984) attributed the increase in cation and anion exchange capacity of Andisols to the ionic strength charging of variable charge surfaces with differing ZPCs. When batch adsorption experiments were conducted with separate phases, Wada (1984) observed that an increase in concentration and adsorption of either the anion, in the case of aluminum hydroxide, or the cation in the case of silica, resulted in a shift in the solution pH towards the ZPC of the sorbing phase. If the two solid phases were combined, the shift in solution pH for each of the surfaces was neutralized by the adsorption reaction of the other surface.

The highly weathered sediments studied here generally display the same type of behavior described by Wada (1984) for adsorption on a combination of surfaces with differing ZPCs, but several observations indicate that Al exchange and hydrolysis may play an important role in controlling adsorption and transport of ionic solutes. Even though silica has a low ZPC ($\text{pH} \approx 2.0$) and can act as a variable charge adsorption site for cations at the pH of the present study, the coarse texture and low reactive surface

area make it unlikely that the quartz sand fraction can account for the cation adsorption observed in the column experiments (Fig. 5B). In batch adsorption experiments "salt sorption" is often accompanied by a reduction in neutral salt extractable Al (exchangeable Al) (Pearce, 1994). Exchangeable aluminum can act as a sink for both solution cations and hydroxyls generated during adsorption of tracer anions on variable charge surfaces, thus countering any shift in the solution pH that accompanies anion adsorption and reducing the exchange equivalency of the Al species. When the anion adsorption potential within the matrix was exceeded at high ionic strengths, Al exchange and hydrolysis continued and a decrease in pH was observed regardless of the treatment solution anion.

The results of this study suggest that highly-weathered sediment should be viewed as mixed variable/constant charge systems that are at, or very near their ZPNC; and therefore, both the sign and magnitude of surface charge are sensitive to changes in solution composition, i.e., cation/anion type, pH, and ionic strength. In one-dimensional column experiments, reliable independent estimates of basic model parameters such as flow rate and porosity make the recognition of non-conservative behavior more straightforward, but at the field scale it may be impossible to distinguish between adsorption reactions and the physical parameters that the experiment may be attempting to characterize. Based on breakthrough curves, chemical interactions such as adsorption, ion exchange and even exclusion may be interpreted as having a physical significance (i.e., mixing, flow rate, permeability, immobile/mobile regions etc.). If the transport of an adsorbed ionic species is assumed to be conservative ($R=1$), calibration of the advection-dispersion model of solute transport would underestimate flow velocity or overestimate formation porosity. It is easy to visualize that pulse tracer solutions would show extreme "non-conservative" behavior as dilution and hydrodynamic dispersion are combined with the ionic strength dependent adsorption of the tracer as it moved through the region of interest, thus negating the validity of derived

transport parameters.

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Figure 1. Schematic diagram of experimental column setup. The pressure drop along the column and the effluent pH, turbidity, and electrical conductivity (EC) were monitored continuously using a PC.

Figure 2. Effluent EC (A) and pH (B) breakthrough for various 0.001 N salt solutions.

Figure 3. Effluent EC (A) and pH (B) breakthrough for various 0.1 N salt solutions.

Figure 4. Relative cation breakthrough (C/C_0) for mixed cation solutions (250 mg L⁻¹ Na, 15 mg L⁻¹ Ca, 5 mg L⁻¹ Mg) prepared from chloride (A) and (B) sulfate salts. Open symbols refer to solutions with a pH of 5.6 and closed symbols refer to solutions with an adjusted pH of 10. The resulting effluent pH (C) for sulfate and chloride solutions ($\approx$ inlet pH 5.6).

Figure 5. Bromide breakthrough in the coarse textured sediments (A) and acid-washed sand (B). Figure A shows the influence of concentration and cation valence on Br breakthrough.

CHAPTER V:**Physicochemical Controls on Non-Conservative Anion Migration in
Coarse-Textured Alluvial Sediments**

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ABSTRACT

Three sandy subsurface materials and a sandy surface soil (Orangeburg Series) from the Upper Coastal Plain, were used to assess the influence of mineralogy and surface chemistry on the determination of physical transport parameters using ionic tracers. The clay mineralogy of the surface soil consisted primarily of kaolinite, hydroxy-interlayered vermiculite, and gibbsite, while the dominant clay mineralogy of the subsurface materials consisted of kaolinite, goethite, and mica (illite). Repacked columns of the four differing strata were leached with tritiated ($\approx 200 \text{ pCi mL}^{-1}$) Bromide solutions, either MgBr_2 or KBr , of varying ionic strengths ($0.1\text{-}0.001 \text{ M}$). Pore water velocities estimated by bulk density and mass flux were consistent with those estimated from tritium breakthrough. In contrast, Br^- breakthrough differed drastically within the four materials and was altered by experimental conditions (sample drying, carrier cation, etc.). The retardation for 0.001 M KBr varied from 0.94 for the surface soil to 2.15 for the subsurface materials and increased with increasing Fe oxide content. For the subsurface samples, Br^- was retarded to a greater degree in the presence Mg^{2+} compared to K^+ . In contrast, oven drying the sample reduced the degree of Br^- retardation observed for the subsurface materials. These results indicate that retardation can vary dramatically within materials of similar texture, mineralogy and origin. The apparent conservative behavior of an ionic species under a given set of conditions (mineralogy, pH, ionic strength, scale size, predominant counter ion) does not automatically ensure that transport will remain conservative as those conditions are altered by changes in experimental design or unforeseen circumstances encountered at the field scale.

INTRODUCTION

To understand or predict the movement of contaminants in groundwater, tracer experiments are conducted to address one or more of the following objectives: a) estimate the degree of hydraulic interconnection, b) estimate transport parameters (hydraulic conductivity, transport volume, dispersivity, or pore velocity), c) determine a solute/matrix interaction parameter, and d) "calibrate/validate" a flow or transport model (Maloszewski and Zuber, 1992). Implicit in many of these approaches is the assumption that the solute employed as the tracer is behaving conservatively.

Retardation (R) for a given solute is defined as the average velocity of the groundwater (V_w) divided by the average transport velocity of the solute (V_s) of interest:

$$R = (V_w / V_s) \quad [1].$$

In one-dimensional column experiments independent estimates of porosity and water flux make the recognition of non-conservative behavior relatively straightforward, but in field-scale experiments an assumption is made that the position of the tracer plume is a manifestation of the physical properties of the transmissive zone and not a function of chemical interactions between the tracer and the stationary matrix. Bromide and Cl^- are generally considered conservative tracers in most field-scale experiments because of the coarse texture of many groundwater matrices and the presence of negatively charged clay minerals that restrict the pore solution available for transport (i.e. exclusion); thus, increasing the average transport velocity.

Analyses of solute behavior in field-scale experiments has indicated that the dispersive spreading and dilution of a groundwater tracer occurs in a non-Fickian manner; thus, hydrodynamic dispersivity tends to increase with distance from the source (Jensen et al., 1993; Maloszewski and Zuber, 1992; Gelhar et al., 1992). Usually this scale effect is attributed to extreme variations in flow rate and flow path length that are

encountered on the field scale. In addition, dispersivity has been shown to vary greatly for studies conducted within materials of similar geologies and scale sizes (Gelhar et al., 1992), suggesting that factors other than aquifer heterogeneity may have influenced tracer migration. Boggs and Adams (1992) attributed the anomalous transport behavior of Br^- in a coarse-textured alluvial aquifer in Mississippi to the anion exchange capacity of the kaolinite/oxide clay fraction. In a preliminary column experiment using oven-dried material from the same aquifer, Boggs and Adams (1992) failed to observe any significant retardation of Br^- . After completion of the field study where the declining tracer mass was observed (Adams and Gelhar, 1992), a second column experiment was conducted in which sample disturbance was kept to a minimum and inlet solution pH was carefully controlled. Under these controlled conditions, the investigators observed Br^- retardation and hypothesized that both the solution pH and non-disruptive sample treatment were important in replicating the conditions experienced in the field.

In addition to tracer adsorption, several other factors can result in an apparent decline in mass balance, including: i) errors associated with tracer analysis or the method of mass estimation, ii) variations in aquifer porosity, and iii) incomplete or biased sampling practices (Boggs and Adams, 1992). Unfortunately, the extensive sampling required to perform an accurate mass balance analysis is beyond the scope of many field-scale experiments. Considering the time and resources involved in conducting a field-scale experiment, it is surprising that the assumption of conservative anion behavior is often based on a cursory examination of the texture and bulk mineralogy of the aquifer matrix.

As noted by Boggs and Adams (1992), the non-conservative movement of anionic tracers is most often associated with materials that contain appreciable quantities of variable charge minerals such as Fe and Al oxides (Chan et al., 1980; Ishiguro et al., 1992). In an oxide-dominated system, the sign and magnitude of surface charge expressed by the mineral matrix is a complex function of the specific

composition of the mineral assemblage and characteristics of the oxide phase in combination with the pH, ionic strength, and composition of the bathing solution. Laboratory studies have indicated that the degree of non-conservative anion behavior is also a function of the other clay minerals that are present in the system. McMahon and Thomas (1974) observed that Cl^- was retarded in columns that contained significant amounts of citrate-dithionite extractable Fe oxides, but the impact of the Fe oxides on retardation was eliminated or reduced for soils that also contained significant amounts of high-charge clay minerals. Similarly, Bolan et al. (1993) found that sulfate was retained to a greater degree in soils that were high in Fe oxides and contained low amounts of high CEC clays. These observations suggest a condition where exclusion by the constant-charge clay mineral fraction and adsorption by the oxide fraction combine to yield apparently conservative transport behavior.

In well-structured soils, physical disturbance has been shown to influence the transport of both ionic and non-ionic tracers (McMahon and Thomas, 1974). McMahon and Thomas (1974) attributed the early arrival of both tritium and Cl^- in undisturbed soil cores to preferential flow through macropores and suggested that anion transport in well structured soils may not be accurately mimicked in repacked columns. Anion breakthrough in certain soils indicates that the actual spatial arrangement of the clay fraction may influence the transport of an adsorbed ionic tracer. McMahon and Thomas (1974) observed greater Cl^- retention in an undisturbed Pembroke silt loam than in the same repacked soil, suggesting that the oxide fraction responsible for adsorption was present as coatings on negatively charged minerals (Toner et al., 1989) or the walls of larger transport pores. In the disturbed soil, they hypothesized that a greater portion of the high charge clays were exposed, thus reducing the level of apparent retardation by increasing the degree of anion exclusion.

Some studies have indicated that sample drying may decrease the degree of anion retardation observed in transport experiments (Boggs and Adams, 1992). When

nitrogen transformations were accounted for, Wong et al. (1987) observed that nitrate was retarded to a greater extent for a kaolinitic Ultisol in field lysimeters than in air-dried columns. Although the differences in retardation may have been a function of the differences in scale of the two experiments, Wong et al. (1987) attributed the decrease in anion adsorption to a decrease in the reactivity of the variable-charge mineral fraction with drying. In either case, the deviation in anion transport from conservative behavior is clearly a function of the mineralogic assemblage of the transport matrix and the experimental conditions under which the solute transport study is conducted.

In previous studies, Seaman et al. (1995A, 1995B) reported that the surface charge properties of the coarse-textured alluvial sediments from the Southeastern Upper Coastal Plain, as indicated by mobile colloid generation and ionic solute migration, were dependent on minor changes in solution composition. Neither cations nor anions behaved in a conservative manner and the degree of retardation of any given ionic species was dependent on several solution factors; such as, solute concentration, counterion valence, and solution pH. The retardation of anions and the sensitivity of these systems to changes in solution composition indicated that the variable-charge mineral fraction, such as Fe and Al oxides, were playing a major role in controlling the surface properties of the aquifer matrix. Therefore, the degree of non-conservative anion behavior observed in the field may vary with the relative abundance of these minerals. A failure to recognize these surface/solute interactions could lead to a false interpretation of ionic tracer displacement in terms of physical mechanisms (i.e. aquifer stratification, flow velocity, permeability, dispersivity, etc). The objective of the present study was to investigate the influence of variable mineralogy encountered over a few meters within a given aquifer on the degree to which anions are retarded. Solute breakthrough experiments were conducted using a surface soil and four subsurface materials typical of coarse-textured, highly-weathered sediments of the Upper Coastal Plain. Additional solution treatments focused on the influence of cation valence, tracer

concentration, and sample treatment on the breakthrough of anionic tracers under relatively low ionic strength conditions that are more relevant to dilute groundwater systems experienced in many field-scale studies.

MATERIALS AND METHODS

Sample Collection and Characterization

The surface soil, a member of the Orangeburg Series (Typic Paleudult), was collected from a mixed coniferous/deciduous forested area, while the three subsurface materials representative of the highly-weathered sediments of the Upper Coastal Plain were collected from a deep erosional exposure on the Department of Energy's Savannah River Site (Aiken, SC). The dried crust present on the subsurface exposure was removed to reveal the moist material below. Three distinct bulk samples were collected over a 3 meter depth span reflecting only minor changes in appearance and texture. The mineralogy and texture of the subsurface samples were consistent with numerous cores taken from the vadose zone, the water table aquifer, and the upper zones of the first confined aquifer (McBean Formation) on the Savannah River Site. The pH and electrical conductivity (EC) of each sample were determined in 2:1 ratio (solution/sample) with deionized water. Particle-size distribution was determined by the micro-pipette method using a dispersing agent (Miller and Miller, 1987). Dry sieve analysis was performed on the bulk samples to estimate formation permeability (Driscoll, 1986).

For mineralogical characterization, the clay fractions of the bulk samples were dispersed by saturation with Na_2CO_3 (pH 10) and separated by centrifugation (Jackson, 1979). Aliquots of the clay concentrates were plated on petrographic slides using the Drever method (1973), and analyzed by x-ray diffraction from 2 to $30^\circ 2\theta$ using Cu K α radiation and a Phillips Norelco diffractometer equipped with a graphite

monochrometer. Treatments consisted of Mg, Mg-ethylene glycol (Mg-EG), and K saturation, the latter of which was heat treated at 110, 300 and 550 °C prior to x-ray analysis. The combined sand and silt fractions were powder mounted on aluminum box slides and analyzed by x-ray diffraction from 3 to 60 °2 θ . Iron oxide content was estimated by citrate-dithionite-bicarbonate (CDB) extraction (Mehra and Jackson, 1960), and amorphous Fe-oxide content was estimated by ammonium oxalate (AO) extraction in the dark (Jackson et al., 1986).

Column Methods

Moist samples were packed into columns as previously described (Seaman et al., 1995A), slowly saturated from the outlet with deionized water ($\approx 0.1 \text{ mL min}^{-1}$), and then leached with a given treatment solution at a constant Darcy velocity of $\approx 0.72 \text{ m d}^{-1}$. Treatments consisted of tritiated ($\approx 200 \text{ pCi L}^{-1}$) KBr or MgBr_2 solutions ranging in concentration from 0.001 to 0.1N. Effluent pH and EC were monitored continuously and fractions were collected for Br^- and tritium analyses as described previously (Seaman et al., 1995B). Only one breakthrough experiment was conducted in a column before the matrix was replaced with fresh sample.

Tracer Data Analysis

For simplicity, the one-dimensional equilibrium deterministic transport model of Parker and van Genuchten (1984) was used to estimate the transport parameters in the column experiments. Model derived estimates of velocity (V) and the dispersion coefficient (D) based on tritium breakthrough were used to calculate a Br^- retardation factor for each column. The lack of extensive tailing for tritium breakthrough and leachout curves indicated that a one-region model was sufficient to describe the physical transport behavior.

RESULTS AND DISCUSSION

Sample Characterization

The physical and chemical characteristics of the four materials used in this study are summarized in Table 1. All four materials were very coarse in texture and ranged from ≈ 85 to 95% sand. Dry-sieve analysis, a method often used to estimate aquifer permeability, tended to underestimate the clay (mud) content of the subsurface materials. Based on the sieve analysis, materials that were high in gravel and coarse sand and low in clay content yield the highest permeability.

For soils, citrate-dithionite-bicarbonate extraction has been used to estimate total Fe oxide content without differentiating specific Fe mineral phases (Schwertmann and Taylor, 1989). In contrast, ammonium-oxalate extraction in the dark selectively dissolves poorly crystalline Fe oxides such as ferrihydrite (Schwertmann and Taylor, 1989; McKeague and Day, 1966). In the present study, CDB extractable Fe ranged from a low of 0.15 g Fe/100 g for the surface material to a range of 0.73 to 3.59 g Fe/100 g for the subsurface materials. Of the Fe oxides present in the subsurface materials, very little was oxalate extractable indicating that the Fe was found primarily in crystalline oxide forms.

Table 1. Physical and chemical characteristics of samples used in the column experiments.

	Sample			
	A	B	C	D
pH*				
KCl	3.90	4.40	4.30	5.03
water	4.61	5.37	5.33	5.18
EC ($\mu\text{S}/\text{cm}$)	53.93	5.86	5.47	8.57
Extractable Fe	(g Fe 100g ⁻¹)			
CDB	0.15	0.73	1.11	3.59
Ammonium Oxalate	0.03	0.01	0.01	0.02
Particle Size Dist.**	%			
Sand (50-2000 μm)	85.5	94.9	91.1	87.2
Silt (2-50 μm)	7.8	0.8	0.5	4.5
Clay (<2 μm)	6.6	4.3	8.4	8.3
Dry Sieve Analysis†	%			
Gravel	0.36	0.08	0.02	0.51
Sand	95.01	99.02	98.71	98.91
Mud	4.64	0.90	1.27	0.59
	m d^{-1}			
Estimated Permeability	20.78	15.21	11.68	23.97

A = Orangeburg Surface Soil

B-D = Subsurface Samples (see Fig. 6)

*2:1 soil/solution ratio

**Miller and Miller Method (1987)

† as described by Driscoll (1986)

Sample Mineralogy

Kaolinite was found to be the primary clay mineral constituent of all four materials, but the clay fraction of the Orangeburg sample (A) also consisted of hydroxy-

interlayered vermiculite with trace amounts of gibbsite and quartz. For the subsurface materials, the Mg- and Mg-EG saturated patterns failed to show any discernible 1.4-1.8 nm peaks characteristic of expandable 2:1 clay minerals, but consistently displayed the peaks for kaolinite (0.7 nm), mica (1.0 nm) and goethite (0.415 nm) (Fig. 1). The mineralogy of samples B and C was similar; therefore, only one diffraction pattern is included in Fig. 1. The higher Fe oxide content for sample D, as measured by CDB extraction (Table 1), was also reflected in the general peak broadening and lower peak intensities for the x-ray pattern. The combined silt and sand fractions from each of the four materials consisted almost exclusively of quartz.

KBr Breakthrough Curves

Tritium derived estimates of pore volume and mean flow velocity were consistent with the estimates based on bulk density of the material and inlet mass flux: values typically differed by less than 5%(not shown). In spite of the coarse texture of the four materials used in the column experiments, tritium normalized Br⁻ breakthrough differed dramatically for each of the materials (Fig 2A). Breakthrough in the surface soil (sample A) was extremely consistent with the breakthrough observed for tritium with an R=0.95 (Table 2). The slight degree of exclusion was probably a reflection of the higher CEC mineralogy and organic matter content of the surface soil. For the subsurface materials, the degree of Br⁻ retardation for the 0.001 N KBr influent solutions ranged from 1.57 to 2.15 and increased with increasing CDB extractable Fe oxide content (Table 2). Assuming conservative behavior, calibration of the advection-dispersion equation to breakthrough of Br⁻ would underestimate flow velocity or yield physically unrealistic estimates of transport volume. Permeability estimates, based on grain size analysis, tended to underestimate the clay content of the subsurface materials and were poor indicators of potential tracer retardation. Sample A, the sample that displayed the lowest retardation factor (<1), and sample D, the sample with the highest retardation

factor possessed the highest estimated permeability.

Table 2. CXTFIT estimated retardation of Br⁻ for various sample and experimental conditions.

Treatment	Sample*			
	A	B	C	D
0.001 N KBr	0.95	1.57	1.80	2.15
0.001 N KBr (OD)**		1.45		1.98
0.001 N MgBr		1.82		2.51
0.010 N KBr				1.35
0.100 N KBr				1.08

R>1 = sorption

R<1 = exclusion

*Calibrated to the breakthrough of tritium using CXTFIT (Parker and van Genuchten, 1984)

**Oven dried sample (110 °C)

As observed for the retardation of Br⁻ in the subsurface materials, anion adsorption is usually attributed to the Fe and Al oxide fraction (Toner et al., 1989). Surface charge is generated for these minerals by the excess adsorption of the potential determining ions (H⁺ and OH⁻) at the solution/surface interface; thus, the sign and magnitude of surface charge can vary with the concentration and activity of these two species, i.e. pH (Sposito, 1984; Uehara Gillman, 1981). Most Fe and Al oxides possess a zero point of charge (ZPC) in the pH range of 7 to 9, and therefore, display a net positive charge under pH conditions below these values (Sposito, 1984). Even though the net-positive charge on an oxide surface increases with decreasing pH, the effluent pH expressed by the four column materials was a poor indicator of Br⁻ adsorption (Fig 2B). Sample A, the surface sample displaying Br⁻ exclusion (R<1), actually displayed the lowest effluent pH of the four materials evaluated, and the effluent pH increased with increasing degree of Br⁻ retardation for the subsurface materials. At first these observations may seem contradictory; however, the effluent pH and degree of Br⁻ retardation displayed by the four materials was a reflection of the reactions

responsible for ion retardation as influenced by the differences in mineralogy between the four samples.

At a given pH, the net charge on a variable-charge surface will increase with increasing ionic strength, but any net adsorption of an ionic solute will have a tendency to shift the solution pH towards the ZPC for the adsorbing mineral (Uehara and Gillman, 1981). In the case of Br^- adsorption, an upward shift in pH would be expected. However, this assumes that Br adsorption is the only reaction occurring within the column. Previous studies indicated that hydrolyzable Al dominates the cation exchange complex of these highly-weathered materials (Seaman et al., 1995A; 1995B). As the tracer solution passes through the column and the ionic strength increases, Al exchange with tracer solution cations followed by hydrolysis, also known as the salt effect, will have a tendency to lower the solution pH. For the surface soil, the reactions of Al exchange and hydrolysis control the solution pH because of the lower Fe oxide content. For the subsurface materials, the upward shift in pH resulting from anion adsorption countered any Al exchange and hydrolysis reactions; thus, a higher pH was observed for samples displaying a greater degree of Br^- retardation.

Influence of Experimental Methodology

Carrier Cation

When Mg^{2+} was used as the carrier cation for the tracer solutions in the subsurface materials, Br^- breakthrough was retarded to a greater extent than in the presence of K^+ (Fig. 3). In each case, the greater retardation of Br^- in the presence of Mg^{2+} coincided with a lower effluent solution pH than the value expressed for the K^+ treatment and reflects the greater ability of the divalent cation to replace Al on cation exchange sites or form more specific bonds with variable-charge oxide surfaces (column data not shown). This lower pH combined with specific adsorption of the divalent cation to the variable charge oxide fraction can increase surface positive

charge and anion exchange capacity of the oxide (Bleam and McBride, 1984).

In contrast to the influence of the divalent cation, oven drying the subsurface samples prior to conducting the Br^- breakthrough reduced the degree of retardation observed (Table 2). Other investigators have made similar observations (Boggs and Adams, 1992; Wong et al., 1987), but it is difficult to decouple the effect of sample drying from other disruptive sampling practices, such as grinding and sieving, that may alter either the pore morphology or the physical arrangement of the clay/oxide fraction.

Ionic Strength

As observed by Seaman et al. (1995B) and Chan et al. (1980), Br^- breakthrough for highly weathered sediments was dependent on tracer concentration, indicating that a linear adsorption model was inadequate to describe anion retardation (Fig. 4). It is important to note that the tracer concentrations used in this experiment were significantly greater than the ionic strength of native groundwater from this region (Strom and Kaback, 1992). Even at concentrations as high as 0.1 N, Br^- breakthrough was still measurably delayed for sample D. As predicted by Gouy-Chapmann theory of surface charge on variable charge minerals (Uehara and Gillman, 1981), the mass of Br^- adsorbed increases with increasing concentration, but the transport approaches conservative behavior as the concentration of the tracer increases and the ability to experimentally detect small degrees of retardation decreases, indicating that the tracer may appear conservative at one transport scale and not at another (Seaman et al., 1995B). In other words, any solute may be used as a conservative tracer at a given scale if its concentration greatly exceeds the adsorption capacity of the transport matrix.

CONCLUSIONS

The non-conservative behavior of anionic tracers is rarely addressed in field experiments even though the conditions for expression, low ionic strength solutions and

highly leached oxide-dominated systems, are quite common. Chemical interactions such as adsorption, ion exchange, and even exclusion may be interpreted as having a physical significance (i.e. mixing, flow rate, permeability, immobile/mobile regions, stratifications etc.). Even in laboratory column studies, it can be difficult to distinguish between a linear fixation/adsorption process under the influence of a complicated flow regime and a non-linear adsorption process under the influence of a uniform flow regime. Scale effects associated with tracer movement in the field may be due in part to variations in adsorption or exclusion that are encountered as the pulse is diluted within the native groundwater. The aim of this study was not to assert that significant anion retardation occurs in all groundwater environments, but to illustrate that cation and anion exchange are not mutually exclusive conditions and that significant retardation can occur in very coarse textured materials. To ensure that a given solute is behaving as expected, greater attention must be placed on characterization of the aquifer mineralogy, especially the clay fraction. Clearly, pH and texture (permeability) are poor indicators of conservative anion behavior in highly weathered systems and significant differences in retardation can occur within materials of similar mineralogy, texture, and origin. Because of the problems associated with performing accurate mass balance estimates in field-scale experiments, care must be taken to ensure that experimental conditions used for preliminary small-scale solute transport experiments (columns) are analogous to the conditions that are experienced at the field scale. Therefore, the concentration of tracers used in column studies should reflect the lower limits that are likely to be encountered with dilution in the field rather than the initial concentrated pulse.

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Figure 1. Mg-saturated x-ray diffraction patterns for the clay fraction from the surface soil (A) and two of the subsurface samples (B and D).

Figure 2. Bromide breakthrough (A) and effluent pH (B) for 0.001 N KBr tracer solutions. Letters refer to samples in Table 1.

A. Orangeburg
 B-D. Subsurface samples

Figure 3. The influence of cation valence (Mg vs K) on 0.001 M Br breakthrough for sample B and D.

Figure 4. The influence of tracer concentration on Br breakthrough for subsurface sample D.

CHAPTER VI:**Outreach and Educational Activities Associated with the
Colloid Transport Project****Publications:**

Seaman, J.C., P.M. Bertsch, and W.P. Miller. Chemical controls on colloid migration in a sandy aquifer. Environmental Science and Technology (In Press).

Seaman, J.C., P.M. Bertsch, and W.P. Miller. Ionic tracer movement through the highly weathered sediments. Journal of Contaminant Hydrology (In Press).

Seaman, J.C. and P.M. Bertsch. Chapter 11: Determination of physicochemical and mineralogical properties of mobile colloids present in soil and groundwater environments. Lewis Publishers. Ann Arbor MI. Accepted Chapter Proposal for upcoming volume in the "Environmental Particles Series" sponsored by IUPAC.

Publications (Submitted):

Seaman, J.C., P.M. Bertsch, S.F. Korom, and W.P. Miller. Physicochemical controls on non-conservative anion migration in coarse-textured alluvial sediments.
Submitted to the Journal of Ground Water.

Seaman, J.C., P.M. Bertsch, and D.I. Kaplan. Surface chemical controls on colloid generation and mobility in surface and subsurface environments. Invited chapter for Goldschmidt Conference Proceedings (May 24-26, 1995) Published by Geochim. Cosmochim. Acta.

Dissertations:

Seaman, J.C. Physicochemical and mineralogical controls on colloid generation and transport in the highly-weathered sediments of the Upper Coastal Plain.
Submitted to University of Georgia Graduate College, Dec. 1994.

Westinghouse/DOE Documents:

Strom, R.N., B.B. Looney, J.C. Seaman, P.M. Bertsch, and W.P. Miller. Summary report and report: Physicochemical and mineralogical controls of colloid migration and deposition within sediments on the Savannah River Site (WSRC-RP-94-276). Westinghouse Savannah River Company, Aiken SC.

Seaman, J.C. and P.N. Bertsch. Colloid Migration and Deposition Within Sediments on the SRS: Colloid Characterization and Physicochemical Controls of Solute Transport. Submitted to WSRC December 21, 1994.

Abstracts and Presentations (US):

Seaman, J.C., P.M. Bertsch, and D.I. Kaplan. Surface chemical controls on colloid generation and mobility in surface and subsurface environments. Goldschmidt Conference. Pennsylvania State University, May 24-26, 1995.

Seaman, J.C. Invited Seminar: Surface chemical controls on colloid generation and transport within SRS sediments. Environmental Systems Eng. Dept. Clemson University, April 13, 1995.

Seaman, J.C., and P.M. Bertsch. Westinghouse Technology Transfer Conference, Radison Conference Center, Augusta GA, March 14-15, 1995.

Seaman, J.C., P.M. Bertsch, and W.P. Miller. Solute transport through the highly weathered soils and alluvial sediments of the Upper Coastal Plain. American Geophysical Union, 1994 Fall Meeting. San Francisco CA, December 5-9, 1994.

Bertsch, P.M., J.C. Seaman, and D.I. Kaplan. Mineralogical and physicochemical properties of mobile colloids in surface and subsurface environments. Soil Science Society of America, Annual Meetings. Seattle WA, November 13-18, 1994.

Seaman, J.C., P.M. Bertsch, W.P. Miller, and D. Radcliffe. Ionic tracer movement through the highly weathered sediments of the Upper Coastal Plain. Soil Science Society of America, Annual Meetings. Seattle WA, November 13-18, 1994.

Seaman, J.C., PhD Dissertation Defense. Physicochemical and mineralogical controls on colloid generation and transport within the highly weathered sediments of the Upper Coastal Plain. University of Georgia, Environmental Soil Science Dept. Miller Plant Science Bldg. August 11, 1994.

Seaman, J.C., T. Rea, S. Rahe, J. Roberts, and R. Winkler. Physiochemical and mineralogical controls on colloid generation and transport within the highly weathered sediments on SRS. Annual Odum Review Day, SREL, July 1993.

Seaman, J.C., D.E. Radcliffe, W.P. Miller, and P.M. Bertsch. Ion transport and solute breakthrough in a variable charge system. Soil Science Society of America, Annual Meetings. Cincinnati OH, November 7-12, 1993.

Seaman, J.C., P.M. Bertsch, and W.P. Miller. The influence of solution chemistry and flow rate on the generation and transport of colloids in an Fe oxide dominated system. Soil Science Society of America, Annual Meetings. Cincinnati OH, November 7-12, 1993.

Bertsch, P.M. Invited Seminar. Physicochemical controls on colloid generation and mobility in surface and subsurface environments. Div. of Earth Sciences, LBL, University of California, Berkeley CA, November 1993.

Bertsch, P.M. Guest Lecture. Chemical controls on contaminant migration in the subsurface environment. Hydrogeology, University of South Carolina, Columbia SC, November 1993.

Bertsch, P.M. Invited Seminar. Generation mechanisms and physicochemical characterization of mobile colloids in SRS environments: Implications to facilitated transport. Environmental Restoration Division, WSRC, July 1993.

Bertsch, P.M. Invited Seminar. Generation mechanisms and physicochemical characterization of mobile colloids: Implications for facilitated transport. Dept. of Geology, University of Georgia, Athens GA, May 1993.

Bertsch, P.M. Invited Seminar. Generation mechanisms and physicochemical characterization of mobile colloids: Implications for facilitated transport. Southern Regional Clay Mineralogy Technical Committee S-207, College Station TX, May 1993.

Seaman, J.C., P.M. Bertsch, and W.P. Miller. The role of colloid dispersion in contaminant transport. University System Research Symposium. "Designing Tomorrow's Sustainable Environment Today" University of Georgia, Athens, GA. May 8-9, 1992.

Presentations (International):

Seaman, J.C., P.M. Bertsch, and W.P. Miller. 1994 Ionic tracer movement through the highly weathered soils and alluvial sediments of the Upper Coastal Plain, Southeastern USA. AGU, 1994 Western Pacific Geophysics Meeting. Hong Kong, July 25-29.

Bertsch, P.M., J.C. Seaman, and D.I. Kaplan. Invited Seminar. 1994. Physicochemical controls on colloid generation and mobility in surface and subsurface environments. AGU, 1994 Western Pacific Geophysics Meeting. Hong Kong, July 25-29.

Manuscripts in Preparation:

Seaman, J.C., J. Hopper, and P.M. Bertsch. Effect of flow rate on colloid generation in repacked column studies.

Seaman, J.C., P.M. Bertsch, and T. Rea. Non-conservative transport of fluorobenzoate tracers in highly weathered soils and groundwater systems.

Seaman, J.C., P.M. Bertsch, and W.P. Miller. Mineralogy and composition of mobile colloids from a highly weathered aquifer of the Upper Coastal Plain.

Scheduled Presentations:

Bertsch, P.M., J.C. Seaman, and D.I. Kaplan (Invited Seminar) Mineralogy of mobile colloids in surface and subsurface environments. Clay Minerals Society 32nd Annual Meeting. June 3-8, 1995.

Seaman, J.C. and P.M. Bertsch. Retardation of fluorobenzoate tracers in highly weathered soils and sediments. Annual ASA Meetings, Oct. 29-Nov.3, 1995 St. Louis, MO.

Seaman, J.C., P.M. Bertsch and T. Rea. Solute tracer migration in reconstructed soil profiles. Annual ASA Meetings, Oct. 29-Nov.3, 1995 St. Louis, MO.

Continuing Education Courses:

Analytical electron microscopy. Lehigh University Short Course. Bethlehem, PA. June 1994.

Laser photo-correlation spectroscopy short course. Coulter Corp. Miami, FL. May 1994.

International conference on the migration behavior of actinides and fission products in the geosphere. Sponsors: DOE, University of Florida, University of Georgia (SREL), and the International Atomic Energy Agency. Charleston, SC. December 1993.

Surface area and pore size measurement short course Micromeritics Corp. Norcross,
GA. July 1993. WSRC-OS-95-16

Modeling reactive multicomponent transport through subsurface media. Penn State
University. State College, PA. November 1992.

Summer Undergraduate Intern Program:

Jennifer Hopper. The influence of flow rate on the generation of colloids in surface soils
of the Upper Coastal Plain. UGA/SREL Summer Research Intern Program.
Summer 1993.

CHAPTER VII: GENERAL CONCLUSIONS

Column results confirmed that clay dispersion and migration may be controlled by factors other than sodium levels, such as pH, exchangeable Al, clay mineralogy, and morphology of the clay assemblage. As might be expected in a system dominated by Fe oxides, the generation of a colloidal suspension was observed under two different chemical regimes that correspond to shifts in the solution pH away from the PZC; one due to high Na levels in conjunction with high pH, and a second due low pH and specific cation and anion interactions with the oxide phase.

Analysis of leachate fractions from the column experiments indicated that the movement of both cations and anions through the oxide-dominated system was highly dependent on the composition, pH, and ionic strength of the leaching solution, a factor that most solute transport models do not consider. In addition to controlling contaminant migration, these surface/solute interactions can influence the determination of physical transport parameters using ionic tracers such as bromide. Aquifer parameters that are commonly measured such as grain size (permeability) and pH were poor indicators of the degree of anion retardation, and significant differences in retardation were observed for materials of similar mineralogy, texture, and origin. At low ionic strengths (0.010-0.0005 M) relevant to field-scale transport experiments, neither the cation nor the anion acted conservatively, yielding unrealistic estimates of column porosity or flow rate. At higher ionic strengths, solute breakthrough was essentially conservative regardless of ionic composition.

In one-dimensional column experiments, reliable independent estimates of basic flow model parameters such as flow rate and porosity make the recognition of non-conservative behavior more straightforward, but at the field scale it is difficult to distinguish between influence of the various experimental factors and the physical parameters that the experiment is attempting to characterize. The apparent conservative behavior of an ionic species under a given set of conditions (mineralogy, pH, ionic strength, scale size, predominant counter ion) does not automatically ensure that transport will remain conservative as those conditions are altered by changes in experimental design or unforeseen circumstances that are encountered at the field

scale.

Most groundwater matrices are viewed as having a net negative surface charge. Therefore, solute transport experiments are conducted using anions as conservative tracers and colloid transport experiments are biased towards factors that enhance the movement of negatively charged colloids through a negatively charged matrix. This model may be valid in systems that contain appreciable quantities of high charge clays or where organic coatings control surface charge expression, but may not be applicable in highly weathered systems that are controlled by Fe oxides. Extremely disturbed (grinding) samples are often saturated with high ionic strength solutions in an attempt to have a greater control over the factors that influence solute transport and clay dispersion, but these conditions may produce model parameters inappropriate to conditions in the field. The result of cation saturation and disruptive sample treatment is that the initial dynamic interactions of Al exchange and hydrolysis with a spatially distributed mineralogy are overlooked. Also, without experiments designed to evaluate alternative mechanisms for colloid stabilization and proper surface charge characterization of the mobile phase, e.g., electrophoretic mobility, dilute colloidal suspensions produced in column experiments may be incorrectly attributed to factors such as column packing, dissolution of cementing agents, or native Na levels.