

Field studies of in situ colloid mobilization in a Southeastern Coastal Plain aquifer

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Abstract. The release of colloids to groundwater was investigated in situ in an iron-oxhydroxide-rich, sandy aquifer. Groundwater amended with various solutes was injected into and immediately withdrawn from the shallow aquifer. Turbidity and colloid composition were monitored in the retrieved injectate. The response of the aquifer material to the amendments generally mimicked that observed in an earlier study using packed columns containing the sediment, demonstrating the viability of the single-well method for testing colloid mobilization in situ. The decline of turbidity in the retrieved injectates with increasing withdrawal volume was analyzed to determine a "reaction order" n , describing the redeposition of mobilized colloids to the immobile matrix. Differences in the reaction order for the amendments tested presumably indicated the effectiveness of these amendments to generate repulsive colloid-immobile matrix interactions.

1. Introduction

The mobilization of aquifer fines due to perturbations in groundwater composition is an important process which must be considered in contaminant transport models [Buddemeier and Hunt, 1988; McCarthy and Degueudre, 1993; Ryan and Elimiech, 1996; Roy and Dzombak, 1997]. Field and laboratory evidence indicate that various toxic metals [Puls and Powell, 1992; Newman et al., 1993; Kaplan et al., 1995], actinides [Short et al., 1988; Penrose et al., 1990; Kaplan et al., 1994], and hydrophobic organic contaminants [Gounaris et al., 1993] associate with such clay-sized solids. Thus mobilization and subsurface transport of these aquifer fines may enhance the transport of the associated contaminants.

A variety of geochemical processes are thought to induce mobilization of aquifer fines. Dissolution of carbonate [Gschwend et al., 1990; Ronen et al., 1992] and iron oxide [Ryan and Gschwend, 1990] cements has been suggested to explain the presence of aluminosilicate-rich colloids in some groundwaters. In addition, numerous laboratory studies on natural and synthetic aquifer materials have found that chemical perturbations which promote particle-particle repulsive interactions among the fines can mobilize colloids. For example, lowering the ionic strength of pore fluids increases the electric double layer thicknesses surrounding solid surfaces. If juxtaposed surfaces possess similar charge, electrostatic repulsion will be enhanced, possibly inducing mobilization of the solids [Goldenberg and Margaritz, 1983; McDowell-Boyer, 1992; Roy and Dzombak, 1996]. Acidic or basic pH [Cerdeira, 1987; Ryan and Gschwend, 1994; Seaman et al., 1995] or dissolved organic matter [Kaplan et al., 1993], anionic surfactants [Ryan and Gschwend, 1994], and other adsorbates may alter the surface charges of solids, producing juxtaposed surfaces with similar surface charge and enhanced repulsive interactions among aquifer fines.

Packed columns have been used widely to study colloid mobilization behavior in sediments. However, field-based study of

the phenomenon is limited [Kaplan et al., 1993]. To this end we used a single-well, injection-withdrawal method to study colloid mobilization behavior in situ in a southeastern coastal plain aquifer. In these in situ experiments, known volumes of groundwater were slowly injected into the aquifer over a period of several hours via wells screened and packed off at a discrete depth. The injected slugs of groundwater had been amended with a number of solutes whose ability to induce mobilization had been studied in packed-column experiments [Swartz and Gschwend, 1998]. The injected slugs of amended groundwater were then immediately retrieved by reversing flow. "Control" experiments were also performed with unamended groundwater to determine the levels of turbidity produced by physical perturbation inherent in the flow reversal process.

The objective of the current study was to determine whether in situ colloid-release behavior followed patterns similar to those that had been observed in packed-column experiments [Swartz and Gschwend, 1998]. From the results of these column experiments we hypothesized that solutes which break bonds between amorphous iron oxyhydroxides and clay minerals, among which the amorphous iron oxyhydroxides are intimately associated in the sediment [Swartz et al., 1997], would induce colloid mobilization if sufficient electrostatic repulsive forces among these constituents were generated concomitantly [Swartz and Gschwend, 1998]. Furthermore, we wanted to use this in situ methodology to determine if a reaction order describing transport of mobilized colloids varied systematically with the degree of chemical perturbation administered to the aquifer. Both first- and second-order expressions have been found to describe colloid transport in laboratory column experiments [Saiers et al., 1994; Kretzschmar et al., 1997]. The single-well injection-withdrawal procedure proved to be an efficient method for testing these hypotheses in situ. Our results indicate that controlled release of colloids to the flowing groundwater may be achievable by perturbing deposits in situ with techniques like the single-well injection-withdrawal procedure. In instances where low-solubility contaminants may be associated with mobilizable aquifer solids, such a method may

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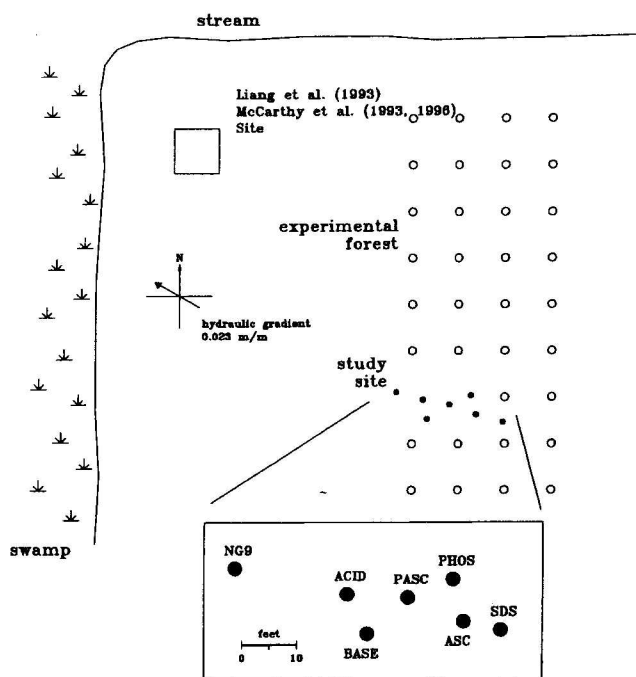


Figure 1. Map of the field site. Depicted are the array of wells emplaced for the injection-withdrawal experiments as well as the location of the studies of *Liang et al.* [1993] and *McCarthy et al.* [1993, 1996]. NG9 marks the location where the samples used by *Swartz et al.* [1997] and *Swartz and Gschwend* [1998] were obtained. The grid of open circles represents the positions of pine trees in an experimental forest plot.

enable improved remediation of the aquifer in comparison to methods such as pump and treat.

2. Methodology

2.1. Site Characterization

The in situ colloid mobilization experiments were conducted in a shallow, unconfined, Southeastern Coastal Plain aquifer located on the grounds of Clemson University's Belle Baruch Forest Science Institute in Georgetown, South Carolina. The 3-m-thick aquifer is composed of a 100,000-year-old marine beach sand and is underlain by a 1-m thick clay layer [*Williams and McCarthy*, 1991]. The sediment is composed predominantly of quartz (approximately 95%). The $<63 \mu\text{m}$ (silt) and $<2 \mu\text{m}$ (clay) size fractions constitute 12% and 2.5% by weight of the sediment, respectively. Phyllosilicate minerals (kaolinite and vermiculite), crystalline (goethite) and amorphous iron oxyhydroxides, and minor amounts of gibbsite and amorphous silica have been identified in the silt- and clay-sized fractions using x ray diffraction, thermogravimetric analysis, selective extraction, and analytical transmission electron microscopy (AEM) [*Swartz et al.*, 1997]. Organic carbon is approximately 0.1% by weight of the bulk sediment [*Holmén and Gschwend*, 1997]. Sediment samples taken from a depth of 2.2 m at location NG9 (Figure 1) in June 1993 and March 1997 were used for the AEM and transmission electron microscopy and column studies [*Swartz et al.*, 1997; *Swartz and Gschwend*, 1998]. The injection depth for all of the wells used in the injection-withdrawal experiments (Figure 1) was centered at 2.65 m below ground surface. This depth was chosen so that the in-

jection depth would be approximately 1 m below the water table, which was located at 1.7 m below ground surface.

The location chosen for our colloid mobilization experiments was approximately 50 m hydraulically upgradient from, and 0.4 m topographically higher than, the location used for study of dissolved organic matter (DOM) transport [*McCarthy et al.*, 1993, 1996] and subsurface iron transformation dynamics [*Liang et al.*, 1993] (Figure 1). The hydraulic gradient in the aquifer is 0.02 to 0.03 SE to NW (Figure 1) [*McCarthy and Degueldre*, 1993; *Yeh et al.*, 1995]. Hydraulic conductivity determinations were not performed at the location of our experiments, although *Yeh et al.* [1995] found hydraulic conductivity to vary from $7.9 \times 10^{-6} \text{ m s}^{-1}$ at a depth of 1.15 m to $7.6 \times 10^{-5} \text{ m s}^{-1}$ at 2.65 m below surface at their site.

2.2. Well and Sampling Apparatus Construction

The well design incorporated a very thin packed-off annulus between the well casing and an insertable injection-withdrawal apparatus so as to minimize the dead volume requiring purging in the well and sampling apparatus (approximately 250 mL total). Details of the well construction can be found elsewhere [*Swartz*, 1998]. Briefly, a 4-inch-ID PVC pipe, with a 3-inch-long slotted screen (slot width equal to 1/1000 inch) centered at the appropriate depth (2.65 m), acted as a traditional well casing which was emplaced as a hole was hand augered. For all wells augered for this study, the bottom of the 4-inch-ID casing was advanced to approximately 3.2 m. After the 4-inch-ID casing was emplaced, a removable apparatus, fabricated from two lengths of 3-inch-ID PVC pipe joined by a 4-inch-long PVC coupling, was inserted into the casing. When inserted, the center of the coupling was aligned with the center of the slotted interval in the well casing (Figure 2). The coupling was plumbed with barbed fittings, and 1/8-inch-ID polyethylene tubing joined in a manifold arrangement to produce a radial injection-withdrawal system around the perimeter of the coupling (Figure 2). This "screened interval" on the coupling was bounded above and below by packers fashioned from rubber inner tubes and inflatable from ground surface, creating a thin annular injection zone between the casing and the coupling (Figure 2).

A single length of 5/16-inch-ID tygon tubing was connected to the manifold distribution system. Within the 5/16-inch-ID sample line tubing was a length of 1/8-inch-OD stainless steel tubing (high-performance liquid chromatography grade, Alltech Associates). Both of these lines extended up through the interior of the 3-inch-ID PVC pipe and connected the manifold at the screened interval to a brass "T" fitting at ground surface (Figures 2 and 3). The "T" fitting separated the stainless steel and plastic lines (Figure 3, inset). This arrangement allowed samples to be obtained from the manifold location, using the stainless steel line, so that the initial conditions of the injectate could be monitored during the injection phase of the experiments.

Beyond the "T" fitting, the plastic line was connected to a sampling apparatus and a peristaltic pump (Figure 3). This sampling apparatus utilized teflon stopcocks and tubing, a vacuum gauge, and a 125-mL polyethylene sample bottle to collect discrete samples of well discharge (Figure 3). This sampling apparatus allowed pumping to be stopped without losing the column of water held in the line from the screened interval up to ground surface while sample bottles were exchanged. After bottle exchange the pump would be restarted, and the vacuum gauge would be monitored until the system approached the

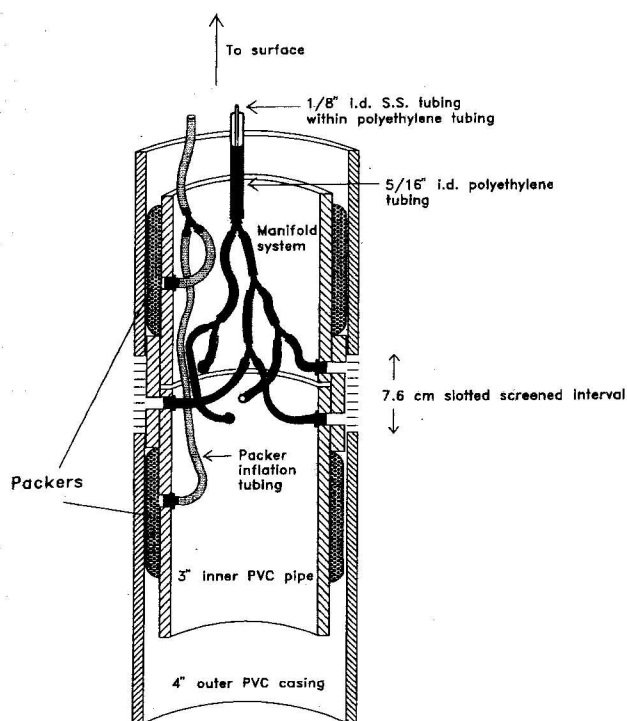


Figure 2. Schematic diagram of the well construction. Each well consisted of (1) a 4-inch-ID PVC outer casing with a 3-inch-long slotted screen (1/1000 inch) and (2) a 3-inch-ID inner well apparatus which included a tubing manifold distribution system (i.e., the "screened interval") for injection and withdrawal of water from the aquifer bounded by inflatable packers.

appropriate vacuum. The upstream stopcock would then be reopened and discharge recommenced. The entire exchange procedure required approximately 30–40 s.

2.3. Experimental Procedures

2.3.1. Well and injectate preparation. Each new well was first "developed" by conducting three to four short (2-L volume) injection-withdrawal sequences (at 100 mL min^{-1}) in succession to rid the well of any loose material created by well emplacement. The first well in which experiments were conducted (BASE, Table 1) was not "developed" before commencing with the first injection-withdrawal experiment (BASE-BC1, Table 1) for that well.

An amount of groundwater sufficient to complete the sequence of experiments designated for that well was then collected (also at 100 mL min^{-1}) after determining that baseline turbidity (≤ 0.08 nephelometric turbidity unit (NTU)) had been reached. The volume of groundwater collected and prepared for reinjection was generally 20 L, although only 11.5 L were injected. Each well was then pumped overnight at 100 mL min^{-1} before beginning the first experimental injection-withdrawal sequence for that well.

A conservative tracer (reagent grade NaBr) was added to each injectate volume to allow calculation of a mass balance on the amount of injectate retrieved and to determine which retrieved samples of each injectate were affected by dispersive mixing with formation water. NaBr was added to a concentration of $500 \text{ } \mu\text{M Br}^-$, 3 orders of magnitude greater than the ambient concentration of Br^- in the groundwater (440 ± 60

nM). Depending on the experiment, various chemically perturbing solutes were added to the groundwater as well. Reagent grade l-ascorbic acid, sodium phosphate monobasic (NaH_2PO_4), and ultrapure sodium dodecyl sulfate (SDS) (GibcoBRL) were used. NaOH and HCl were used to adjust pH.

2.3.2. Injection-withdrawal procedure. An injection was commenced by stopping the pump (discharge of groundwater from a well was maintained continuously once the "development" sequence discussed in section 2.3.1 had been carried out), connecting the pump to tubing feeding from the carboy, and switching the pump back on in reverse (injection) mode. All experiments were conducted at a pumping rate of 100 mL min^{-1} , which corresponded to a seepage velocity of approximately 2.0 m d^{-1} at the well screen, calculated using the area of the well screen and a porosity of 0.30. Depletion of the carboy was monitored until the appropriate volume of groundwater had been injected. Five 10-mL samples were taken from the stainless steel line by syringe during the course of the injection in order to obtain initial concentrations of the conservative tracer and other added solutes and to monitor pH of the injectate close to the point of injection. Flow was then stopped, and the pump was disconnected from the carboy feed tubing and turned back on in discharge mode. The dead volume of the well and sampling apparatus was allowed to pass through the system before commencement of sample collection.

During the withdrawal phase a 125-mL sample was collected for every 500 mL of discharge up to 25-L total discharge. Samples were then usually taken every 2 L up to 31-L total discharge and then every 5 L to 10 L thereafter until background levels of the conservative tracers were reattained (usually 45 to 50 L for attainment of background Br^- or 4 to 5 times the volume injected). After that, pumping was maintained at 100 mL min^{-1} until the next injection experiment in the sequence was commenced for that well (usually after approximately 120 L, or 10 times the previous injection volume, had been discharged).

2.3.3. Sample analysis. For the samples collected during the withdrawal phase of experiments, turbidity (Ratio X/R instrument from Hach) was measured in the field in subsamples (30 mL) poured from the 125-mL sample bottle into a turbidity sample cell. Because the groundwater was oxic (see section 3), there was little danger of creating artifactual turbidity by briefly exposing the samples to the atmosphere in transferring them to the turbidity sample cell [Backhus *et al.*, 1993]. The pH was measured with a combination electrode and a temperature compensation probe (Orion) in a separate subsample. A 35-mL subsample was also archived for later analysis.

A 2-mL subsample from each archived 35-mL sample of discharge was passed through an acid-pretreated 30-nm pore-size membrane (Osmonics) in the field. Dissolved metal concentrations in these filtered subsamples were determined later using graphite furnace atomic absorption (AA) spectroscopy (4100ZL, Perkin Elmer). Bromide concentrations were measured by either ion chromatography (Dionex model 16 ion chromatograph with an anion self-regenerating suppressor column) or inductively coupled plasma mass spectrometry (VG Plasmaquad KP-20, Visions Instruments).

In appropriate archived samples, colloidal Al/Fe mole ratios were determined by first digesting a 1-mL subsample with 0.15 to 0.30 M hydrofluoric acid (HF) for 72 hours, followed by quantification of Fe and Al by (AA) analysis. This analysis was

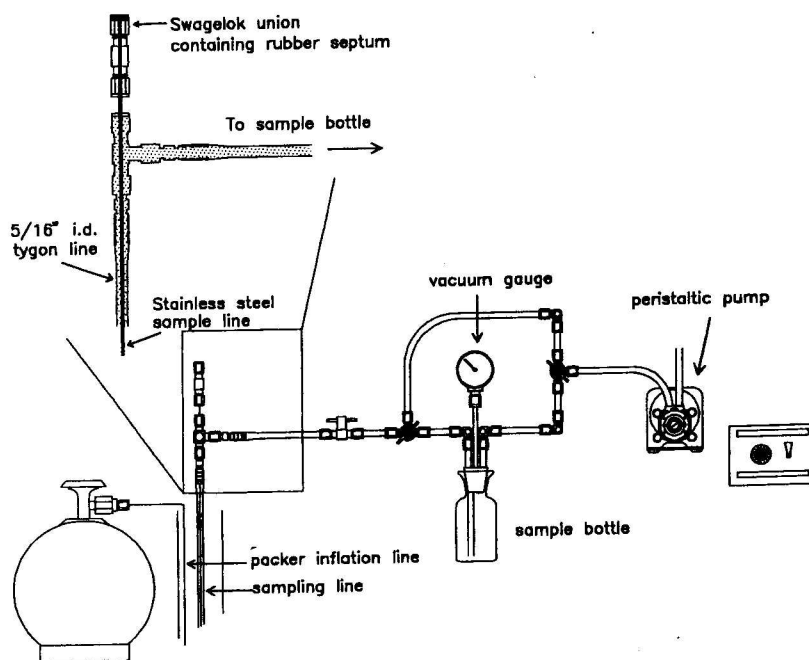


Figure 3. Schematic diagram of sampling apparatus at ground surface, including the "T" fitting separating the 1/8-inch-OD stainless steel line from the 5/16-inch-ID polyethylene line that descends to the screened interval (see inset). Stopcocks allowed vacuum to be maintained in the sampling line while sample bottle exchange took place.

performed on subsamples from at least the first eight archived samples of an experiment.

Thermal analysis (Perkin Elmer TGA7) was performed on colloidal material when sufficient mass was able to be concentrated from what remained of archived samples after all other analyses described above had been conducted. The sample was centrifuged at 23,000 g for 30 min, the supernatant was decanted, and the residue was allowed to air dry. Approximately 2 mg samples of the dry, concentrated solids were heated from 30° to 800°C at 10° min⁻¹.

The initial groundwater composition (dissolved metals, dissolved organic carbon, O₂, alkalinity, and conductivity) was also assessed using samples obtained from each well before any injection-withdrawal experiments were conducted in that well. Dissolved metals (Fe, Al, and Si) were measured in the same manner as for the experimental samples. Dissolved O₂ was measured colorimetrically (Chemets, Chemetrics), and alkalinity was determined by Gran titration with 0.001 N HCl. Non-purgeable dissolved organic carbon was determined by combustion (680°C) and infrared detection (TOC-5000, Shimadzu) of acidified, N₂-purged samples.

2.4. General Organization of Injection-Withdrawal Experiments

Injection-withdrawal experiments were conducted in six different wells on three occasions (Table 1 and Figure 1) in the manner described in section 2.3.2. In one set of experiments, injectate pH was sequentially increased from ambient levels (BASE-BC1, Table 1) to a value of 9.59 (BASE-9.59). In addition, groundwater was amended with 1 mM phosphate (PHOS), 1 mM ascorbic acid (ASC), and a combination of 0.5 mM phosphate and 0.5 mM ascorbic acid (PASC). Groundwater was also amended with either 2 mM or 10 mM sodium dodecyl sulfate, an anionic surfactant (SDS2 and SDS10, re-

spectively), or acidified to pH 2.6 (ACID). These amendments were chosen specifically to test our hypothesis, developed from observations of the sediment's response to these perturbations in column experiments [Swartz and Gschwend, 1998], that lysis of chemical bonds was required to mobilize colloids representative of the entire bulk matrix of this sediment, as will be discussed in detail in section 4.1.

For the BASE, PASC, and SDS tests, control experiments using unamended groundwater (except for the addition of the conservative tracer Br⁻) were carried out both before and after the sequence of amended groundwater injection-withdrawal experiments (Table 1). In the BASE sequence of experiments an additional control experiment (BASE-BC2 with pH 5.13) was conducted prior to the experiment at the highest pH (BASE-9.59). For the ACID, ASC, and PHOS tests, only a "before" control experiment was conducted.

2.5. Analysis of Colloid Transport

We sought to determine whether the transport behavior of the colloids mobilized in our in situ experiments conformed to observations made from column experiments of colloid transport [Saiers et al., 1994; Kretzschmar et al., 1997], that is whether colloid recovery in our effluent varied systematically depending on the groundwater amendment and the level of chemical perturbation applied to the aquifer. To this end we calculated the reaction order describing the mobilized colloid concentration in the retrieved injectate with respect to residence time in the aquifer. To perform this analysis, we first confirmed that turbidity could be used as an analog for the concentration of colloidal solids in our samples. One would expect turbidity and the concentration of colloidal solids to be linearly proportional at a suitably low range of concentration if the composition and size distribution of the light scattering solids remained constant as turbidity varied. We regressed our

Table 1. Experimental Parameters

Experiment	Date	Groundwater Alteration	Mass Br Recovered	Al/Fe Mole Ratio of Mobilized Colloids*
PHOS-BC	October 1997	control (pH _i = 5.35)	0.97	0.8 ± 0.2
PHOS		1 mM NaH ₂ PO ₄ (pH _i = 5.25)	0.96	
SDS-BC	March 1997	control (pH _i = 5.33)	1.02	
SDS2		2 mM SDS (pH _i = 5.33)	0.93	
SDS10		10 mM SDS (pH _i = 5.28)	NM	
SDS-AC		control (pH _i = 5.28)	0.99	
ASC-BC	October 1997	control (pH _i = 5.38)	0.94	1.8 ± 0.2
ASC		1 mM ascorbic acid (pH _i = 5.30)	0.96	
PASC-BC	March 1997	control (pH _i = 5.42)	0.98	2.5 ± 0.6
PASC		0.5 mM NaH ₂ PO ₄ and		
PASC-AC		0.5 mM ascorbic acid (pH _i = 5.78)	0.97	
BASE-BC1	October 1994	control (pH _i = 5.25)	0.96	
BASE-6.88		control (pH _i = 5.19)	0.99	
BASE-7.68		pH _i = 6.88	1.00	
BASE-8.41		pH _i = 7.68	0.97	
BASE-BC2		pH _i = 8.41	1.02	
BASE-9.59		control (pH _i = 5.13)	0.99	
BASE-AC		pH _i = 9.59	0.97	
ACID-BC		control (pH _i = 5.40)	0.98	
ACID	October 1997	control (pH _i = 5.25)	0.97	1.8 ± 0.7
		pH _i = 2.50	NM	

Abbreviations are as follows: PHOS, phosphate; PASC, phosphate and ascorbic acid; SDS, sodium dodecyl sulfate; ACID, acidified (pH 2.6) ASC, ascorbic acid; BC, "before" control; AC, "after" control; NM, not measured; pH_i, pH of injectate.

Al/Fe mole ratios were measured in samples from experiments in which turbidity was noticeably larger than in samples from the control experiments (>1 nephelometric turbidity unit (NTU) difference). Compare these colloidal Al/Fe mole ratios to the Al/Fe mole ratio determined for the bulk matrix (3.2 ± 0.2) from digestion of the <63 μm size fraction [Swartz, 1998].

measured turbidities against their corresponding total Fe contents, derived from HF digestion of the samples, for all samples from experiments to be considered in the transport analysis (i.e., PHOS, ASC, PASC, and BASE-9.59, Table 1). R² values were 0.990, 0.961, 0.997, and 0.969 for the PHOS, ASC, PASC, and BASE-9.59 data, respectively, suggesting that turbidity could, indeed, be used as an analog for colloid concentration for this analysis.

Additionally, we assumed that the single-well injection-withdrawal experiments could be modeled as systems in which the injectate mobilized an amount of colloids (if chemical conditions permitted) upon contacting the sediment around the well screen. This volume of injectate, carrying mobilized colloids, moved outward into the aquifer as recharge continued. The colloidal load was subjected to deposition along this outwardly radiating flow path and again during transport back to the well screen when flow was reversed during the discharge phase. Given this simplified construct of the system, the contact time of the mobilized colloidal load with the stationary aquifer solids (the collector surfaces) was calculated by dividing the volume discharged by the discharge rate and multiplying by 2 (to correct for time spent in the aquifer during the injection and withdrawal phases).

Possessing both a colloid "concentration" (turbidity in NTU) and a suspension contact time with the aquifer for each 500-mL sample withdrawn for each experiment, a reaction order with respect to suspended colloid concentration was deduced using the integrated form of the following rate expression:

$$(dC)/(dt) = -kC^n \quad (1)$$

where k is an overall rate coefficient reflecting the losses of colloids from the mobile phase and n is the reaction order with respect to C , the suspended colloid concentration at a given contact time. Kinetics of reentrainment of the mobilized col-

loids was assumed to be slow in comparison to the timescale of injection and withdrawal of the portion of the injectate used in the reaction order analysis, that is, the portion that was unaffected by dispersive mixing with formation water (see below). This assumption justified neglecting a reentrainment term in the rate expression, as has been done in other studies of colloid transport [Saiers *et al.*, 1994; Kretzschmar *et al.*, 1997]. Logarithmic transformation of the integrated form of (1) provided the following expression:

$$\ln C = \frac{1}{1-n} \ln [C_0^{1-n} + (n-1)kt] \quad (2)$$

where C_0 is the initial concentration of colloids mobilized and $n > 1$. In using (2) for our analysis, we assume that the initial colloid concentration mobilized in each 500-mL volume of perturbing solution injected is the same throughout the 11.5-L injection. This appears to be a reasonable assumption based on calculations which estimate that of the total amount of <2-μm-size fraction in contact with the 500-mL pore space adjacent to a well screen; less than 10% was mobilized by an 11.5-L injection of groundwater with even the most perturbing amendment (PASC, Table 1; see section 3.2).

When the second term within the logarithmic expression on the right side of (2) dominates, the simplified expression

$$\ln C = \frac{\ln [k(n-1)]}{1-n} + \frac{1}{1-n} \ln t \quad (3)$$

is obtained, where n is calculated from the slope, $1/(1-n)$, of the regression of $\ln C$ versus $\ln t$. Only retrieved injectate samples in which the concentration of the Br⁻ tracer was indistinguishable from that of the initial Br⁻ concentration (which included the first 10 samples for each well) were considered for this analysis so that dispersion-induced mixing with formation water would not have to be accounted for. Similar,

but slightly more complicated, constructs which account for dispersion have recently been presented to obtain zero- and first-order reaction rate coefficients from injection-withdrawal experimental data [Haggerty *et al.*, 1998; Snodgrass and Kitanidis, 1998]. Our experimental methodology most closely matches the methodology described by Snodgrass and Kitanidis [1998], whose rate expressions simplify to general zero- and first-order rate expressions when the conservative tracer concentration at a given time equals that of the initial concentration.

3. Results

3.1. Prevailing Groundwater Chemistry

The ambient pH (5.3 ± 0.1) and dissolved O_2 concentration ($140 \pm 9 \mu M$) varied little among the wells, while alkalinity, dissolved organic carbon, and dissolved Fe, Al, and Si were more variable ($26 \pm 10 \mu M$, $92 \pm 21 \mu M$, $130 \pm 100 nM$, $170 \pm 120 nM$, and $370 \pm 120 nM$, respectively). The conductivity ($38 \pm 5 \mu S cm^{-1}$) of the groundwater corresponded to an ionic strength of approximately $0.4 mM$ using the major ions present in the water [Swartz, 1998]. The lack of significant ambient turbidity in the groundwater ($\leq 0.08 NTU$) suggested that colloids were not generally mobilized in this formation under natural conditions by the relatively low ionic strength of the groundwater. Correspondingly, no release of colloids was observed in our packed-column experiments when the sediment was flushed with low ionic strength solutions [Swartz and Gschwend, 1998].

3.2. In Situ Mobilization Results

3.2.1. Injection of phosphate-amended groundwater. Injection of groundwater amended with $1 mM$ phosphate (PHOS) into the aquifer resulted in turbidity in the retrieved samples of injectate that was somewhat elevated in comparison to the control experiment (PHOS-BC) (Figure 4a). For example, the turbidity of the first 500-mL sample withdrawn in PHOS was 12.3 ± 0.2 (error represents 1 standard deviation on sample measurement), whereas the first 500-mL sample withdrawn in PHOS-BC had a turbidity of 4.6 ± 0.1 . By the third sample (1.5 L discharged) the turbidity of the discharge from the phosphate injection had decreased to 2.8 ± 0.1 , whereas control values had decreased to 0.33 ± 0.02 .

After approximately 8 L discharged, when the Br^- tracer began to decrease in concentration (i.e., $V/V_0 = 0.75$, where V is the volume discharged and V_0 is the volume injected, and $C/C_0 Br^- = 0.75$), the turbidity in PHOS rose again from approximately 0.5 NTU to $5.7 \pm 0.1 NTU$ (Figure 4a). Turbidity then declined and rose again to values near 2 NTU before finally falling again to 0.6 NTU at $V/V_0 = 1.1$ (Figure 4a). It is possible that these later turbidity pulses were manifestations of the influx of lower ionic strength water as the injectate (approximately $2 mM$ ionic strength) was replaced by formation water (ionic strength near $0.4 mM$), moving into the injectate-affected zone around the well. Expansion of electric double layers accompanying the decrease in ionic strength may have magnified repulsive electrostatic interactions induced by specific adsorption of the phosphate [Sigg and Stumm, 1980; Liang and Morgan, 1990a] in the zone of influence around the well. This effect has been observed commonly in column experiments, in which turbidity rises during deionized water flushes that follow treatment with a chemically perturbing so-

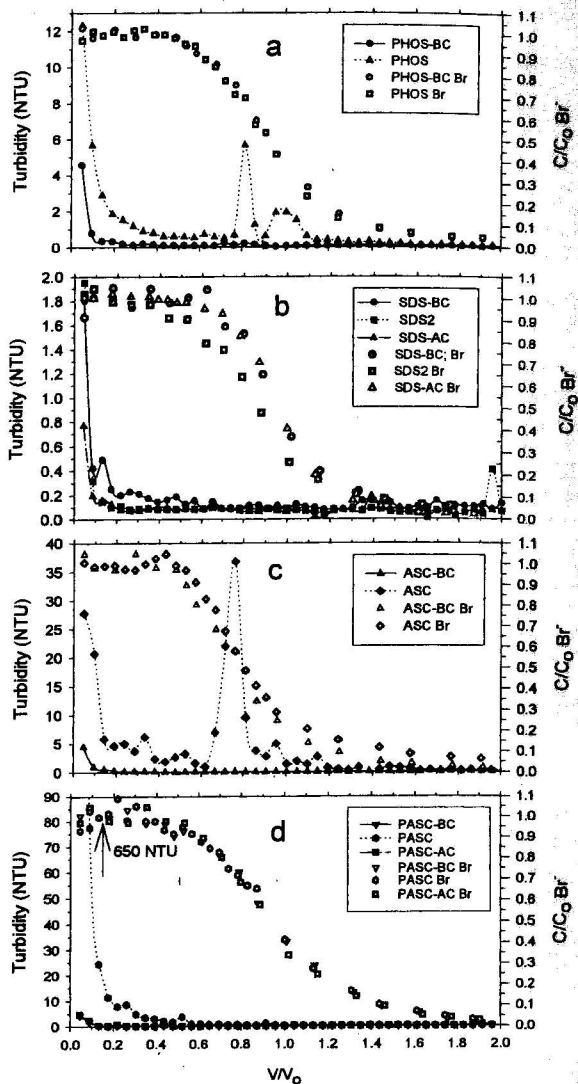


Figure 4. Turbidity and Br^- tracer profiles for experiments (including controls) conducted in (a) phosphate (PHOS), (b) sodium dodecyl sulfate (SDS), (c) ascorbic acid (ASC), and (d) phosphate plus ascorbic acid (PASC) up to $V/V_0 = 2.0$ (volume discharged over volume injected). Data points were collected for each 500 mL discharged from the wells. The profiles of the normalized concentration of the Br^- tracer are presented on the right y axis.

lution [Ryan and Gschwend, 1994; Seaman *et al.*, 1995; Swartz and Gschwend, 1998].

3.2.2. Amendment of groundwater with surfactant. Groundwater amended with $2 mM$ SDS (SDS2) did not produce turbidity significantly different from the levels in either the "before" (SDS-BC) or "after" controls (SDS-AC) (Figure 4b). An injection of groundwater amended with $10 mM$ SDS was also attempted (SDS10) (data not shown). However, the peristaltic pump aggravated foaming of the surfactant solution (the critical micelle concentration of SDS is approximately $8 mM$ in a $1-M NaCl$ solution [Mysels and Mysels, 1965]). The foaming solution physically disrupted the sediment when injected, confounding interpretation of the chemical effect of the surfactant-amended groundwater on colloid mobilization.

3.2.3. Injection of ascorbate- and phosphate/ascorbate-amended groundwater. The turbidity (27.8 ± 0.1) in the first sample of retrieved injectate after injection of 1 mM ascorbic acid (ASC) was greater than that of the control (ASC-BC, 4.5 ± 0.1) (Figure 4c). Turbidity remained at values at or above 2 to 3 NTU to approximately 6 L discharged ($V/V_0 = 0.52$, Figure 4c). At 6.9 L discharged ($V/V_0 = 0.6$ and $C/C_0 \text{ Br}^- = 0.75$, Figure 4c), turbidity began to rise again and reached a peak value of 36.8 ± 0.2 NTU at 8 L discharged ($V/V_0 = 0.75$ and $C/C_0 \text{ Br}^- = 0.6$) before falling to approximately 1 NTU by 12 L discharged ($V/V_0 = 1.04$, Figure 4c). This secondary turbidity pulse appeared at similar values of V/V_0 and reduced Br^- concentration as the secondary pulse which occurred in the 1 mM phosphate injection (PHOS, Figure 4a). Again, this secondary turbidity pulse may have been due to the drop in ionic strength as injectate, diluted with formation water, flushed the affected solids.

Injection of groundwater amended with 0.5 mM phosphate and 0.5 mM ascorbic acid (PASC) produced greater turbidity (>600 NTU in the first 500-mL sample retrieved) than was manifest in the injectates retrieved for either the PHOS or ASC injections (Figure 4d). Turbidity in the first sample of retrieved injectate for both the before and after control experiments (PASC-BC and PASC-AC, respectively) was only approximately 4.5 NTU (Figure 4d). No secondary peak of turbidity occurred in PASC, even though the initial mobilization event was much stronger than that which occurred in PHOS or ASC. Apparently, the injectate-affected solids were not sensitive to contact with the lower ionic strength formation water coming in behind the injectate dispersion front in this experiment.

3.2.4. Amendment of groundwater with base. Turbidity in the first 500 mL of retrieved injectate (27.3 ± 0.1 NTU) from the pH 9.59 injection (BASE-9.59) was considerably higher than turbidity in BASE-8.41 and in the control experiments conducted immediately before (BASE-BC2) and after (BASE-AC) the pH 9.59 injection (Figure 5a). Turbidity decreased gradually to background levels for each of these injections (Figure 5b).

The turbidity in the first 500-mL retrieved samples from experiments BASE-BC1 through BASE-8.41 (Figure 5a) systematically decreased even as pH of the injectate increased. We believe this systematic decrease of the initial turbidity for the successive injectates BASE-BC1 through BASE-8.41 was due to not "developing" the well before beginning the sequence of BASE injections, as discussed in section 2.3. For this reason, turbidity manifest in control experiments BASE-BC2 and BASE-AC was used as a basis for comparison to turbidity observed in BASE-9.59.

The pH of the initial samples retrieved from all of the BASE injections differed from the pH of the prepared injectates (compare pH values of prepared injectates in Table 1 to pH values measured in retrieved samples in Figure 5c). Typically, the aquifer matrix buffering capacity shifted injectate pH downward when injectate pH was elevated above pH 7.0 [Swartz, 1998]. Similar titration of treatment solutions with basic pH occurred in the column experiments [Swartz and Gschwend, 1998]. Conversely, pH in retrieved samples was initially slightly elevated above injectate pH in the control experiments (Figure 5c) [Swartz, 1998].

3.2.5. Amendment of groundwater with acid. Groundwater acidified to pH 2.5 (ACID) did not result in turbidity which was significantly different from the control experiment (ACID-

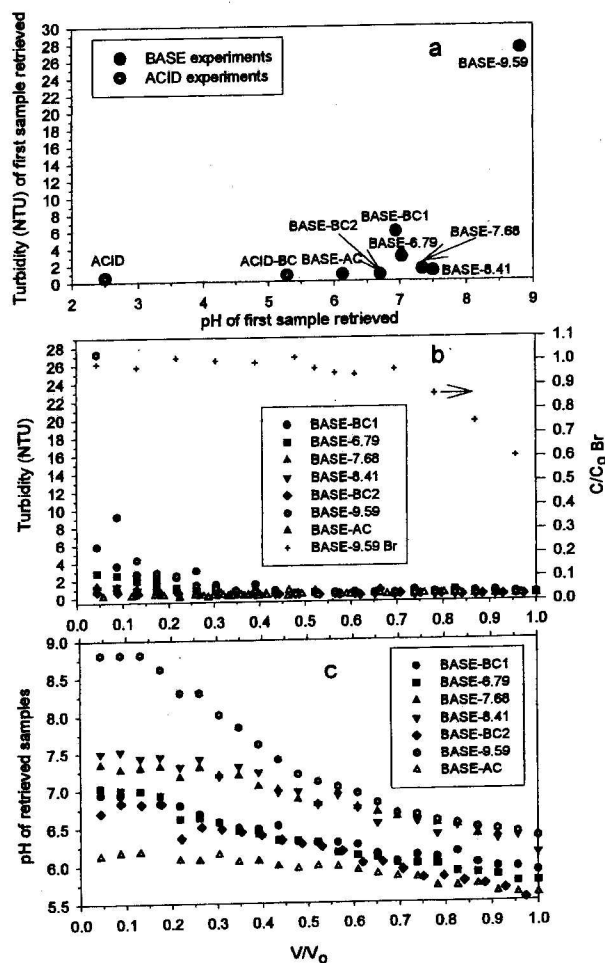


Figure 5. Turbidity and pH data for experiments BASE and ACID. (a) Turbidity for the first 500-mL sample of injectate retrieved. (b) Turbidity profiles (up to $V/V_0 = 1.0$) for the BASE experiments. (c) The pH of the retrieved injectate up to $V/V_0 = 1.0$ for the BASE experiments. For Figures 6b and 6c the legend is the same. The pH indicated in the legend is the pH of the injectate upon injection.

BC), as demonstrated by the turbidity in the first 500-mL samples retrieved from each of these injectates (Figure 5a). The turbidity of the first sample of injected retrieved from ACID (0.59 ± 0.05 , Figure 5a) was actually less than that of the control (ACID-BC 0.78 ± 0.04 , Figure 5a) as were turbidity levels in subsequent samples (data not shown).

4. Discussion

4.1. Comparison of in Situ Behavior to Packed-Column Results

We previously hypothesized that goethite is preferentially mobilized by phosphate treatment in the Georgetown sediment [Swartz and Gschwend, 1998] as only colloids, iron-rich relative to the composition of the sediment bulk matrix (defined by the Al/Fe mole ratio of the $<63\text{-}\mu\text{m}$ -size fraction) were mobilized by treatment with 10 mM phosphate in the packed-column experiments. The average Al/Fe mole ratio (0.8 ± 0.2) of the colloids mobilized in situ by groundwater amended with 1 mM phosphate (PHOS) was very similar to the Al/Fe mole ratio of colloids (0.5 ± 0.3) mobilized in the

deionized water flush following treatment with 10 mM phosphate in the packed-column experiments [Swartz and Gschwend, 1998]. These two average Al/Fe mole ratios are more similar to the Al/Fe mole ratio of the goethite aggregates (0.24 ± 0.8 [Swartz *et al.*, 1997]) than to the Al/Fe mole ratio of the bulk matrix (3.2 ± 0.2 [Swartz and Gschwend, 1998]), suggesting that preferential mobilization of the goethite may have occurred in both the in situ and column experiments. Goethite, which makes up approximately 10% by weight of the $<63\text{-}\mu\text{m}$ -size fraction, was found to occur in discretely organized aggregates in the sediment matrix [Swartz *et al.*, 1997], which may explain why the goethite could be preferentially mobilized. The much lower Al/Fe mole ratio of the colloids in comparison to the bulk suggests that the amorphous iron oxyhydroxide-clay mineral assemblages, with kaolinite being the predominant clay mineral at 45% by weight of the $<2\text{-}\mu\text{m}$ -size fraction, remained predominantly immobile during the phosphate treatments in both the column and in situ experiments. Others have recently observed preferential mobilization of goethite in southeastern coastal plain sediments [Seaman *et al.*, 1995, 1997].

Colloids were not mobilized by treatment of the sediment with a 1 mM phosphate solution in the packed-column experiments [Swartz and Gschwend, 1998]. This discrepancy between the packed-column and in situ mobilization behavior may have been due to the presence of additional adsorbates in the groundwater, such as DOM, which could have acted synergistically with the added phosphate to induce mobilization in the in situ experiments. Carboxyl groups present in DOM are thought to be responsible for observed downward shifts in the pH_{pzc} of iron oxyhydroxides [Liang and Morgan, 1990b]. These additional sorbates would not have been present in the deionized water used to prepare the solutions for the laboratory column experiments. Physical perturbations inherent in the injection-withdrawal procedure also may have contributed to the discrepancy between the packed-column and in situ behavior.

The inability of 2 mM SDS to induce colloid mobilization in the sediment in situ (SDS2) corresponds to the behavior observed in the packed-columns [Swartz and Gschwend, 1998]. SDS would be expected to produce repulsive interactions among matrix constituents by altering the surface charge of positively charged mineral surfaces through admicelle formation [Chandar *et al.*, 1987]. Thus SDS sorption might be expected to enable colloid release similar to that induced by phosphate. Indeed, 2 mM SDS was found to impart greater negative electrophoretic mobility to model goethite colloids than 10 mM phosphate [Swartz and Gschwend, 1998]. That treatment of the sediment with phosphate (both in situ and in packed columns, although only at comparatively higher concentrations of phosphate for the latter case) induced mobilization of iron-rich colloids, while SDS did not, suggests that SDS sorption and admicelle formation on constituent surfaces may have been inhibited. Indeed, phosphate was lost to the aquifer solids to a much greater degree than was SDS [Swartz, 1998].

In the packed-column experiments, colloids compositionally representative of the entire matrix appeared to be mobilized only when adsorbates capable of both (1) breaking bonds between the amorphous iron oxyhydroxides and clay minerals and (2) generating sufficient electrostatic repulsion among matrix constituents were present in treatment solutions [Swartz and Gschwend, 1998]. For example, treatment of the George-

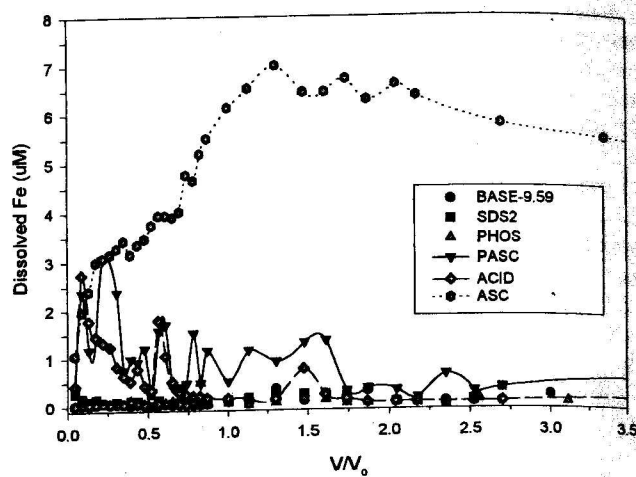


Figure 6. Dissolved Fe (in micromolar) in the retrieved samples of injectate in which particular chemical amendments were made to the groundwater. The PHOS, SDS2, and BASE-9.59 values were generally no larger than ambient concentrations (approximately 130 nM, Table 1). Blank values of dissolved Fe (sampled from the stainless steel line during each injection) for ACID, PASC, and ASC were 680 ± 53 , 300 ± 71 , and 590 ± 230 nM, respectively, due probably to the reaction of these injectates with the stainless steel tubing sampling line. The data for ACID, PASC, and ASC shown in Figure 5 do not reflect correction for these blank values.

town sediment with a solution containing 0.5 mM phosphate (providing electrostatic repulsion) and 0.5 mM ascorbic acid (reductive dissolution of the iron oxyhydroxides and bond breaking) at pH 5.2 was found to induce sustained mobilization (2–3 NTU) of colloids with an average Al/Fe mole ratio of 2.3 ± 0.9 , while 1 mM ascorbic acid at pH 5.2 produced no turbidity [Swartz and Gschwend, 1998]. Similarly, in situ injection of 0.5 mM phosphate to 0.5 mM ascorbic acid amended groundwater (PASC) resulted in mobilization of colloids with an Al/Fe mole ratio of 2.5 ± 0.6 (Table 1). Dissolved Fe concentrations in the PASC retrieved injectate were noticeably larger than the levels observed in the PHOS samples, which remained at ambient levels (Figure 6). The higher dissolved Fe concentrations in the PASC experiment indicated that the ascorbic acid had been effective at initiating dissolution of the iron oxyhydroxides in the aquifer and breaking bonds among the amorphous iron oxyhydroxide-clay mineral assemblages.

PASC was the only experiment in which the archived samples provided enough colloidal mass to perform thermal analysis. Derivative weight loss peaks for the PASC colloids were observed at 300°C (goethite) and 475°C (kaolinite), with the goethite peak being approximately twice the height of the kaolinite peak. Peaks were also observed at the same two temperatures for a sample of the $<63\text{-}\mu\text{m}$ -size fraction of the Georgetown sediment, although the goethite peak was only approximately 0.25 the height of the kaolinite peak in that sample. The thermal analysis data indicate that the PASC colloids were more enriched in goethite relative to kaolinite as compared to the $<63\text{-}\mu\text{m}$ -size fraction (the bulk matrix). The thermal data thus correspond to the trend in the differences observed between the Al/Fe mole ratios for the PASC colloids (2.5 ± 0.6) and the bulk matrix (3.2 ± 0.2).

In situ injection of 1 mM ascorbic acid (ASC) generated colloids in disagreement with the packed-column results

[Swartz and Gschwend, 1998]. The Al/Fe mole ratio of these colloids (1.8 ± 0.2) was more similar to that of the bulk matrix (3.2 ± 0.2) than were the colloids mobilized by PHOS (0.8 ± 0.2). The difference in Al/Fe mole ratios of the colloids generated by the ASC and PHOS experiments probably reflected the ability of the ascorbic acid to break bonds among the amorphous iron oxyhydroxides and clay minerals, as dissolved Fe concentrations in the ASC retrieved injectate was the highest of all the experiments (Figure 6). The ability of 1 mM ascorbic acid to induce mobilization in situ may have been due to the synergistic effect of additional adsorbates in the groundwater and the physical perturbation caused by flow reversal, as discussed above regarding PHOS.

When we treated the sediment with elevated pH (pH 8.8) solutions in packed columns, colloids with an average Al/Fe mole ratio of 1.5 ± 0.5 were mobilized [Swartz and Gschwend, 1998]. Similarly, colloids with an Al/Fe mole ratio (1.8 ± 0.7) were mobilized when groundwater with an initial pH of 9.59 was injected into the aquifer (BASE-9.59, Table 1). Both of these Al/Fe mole ratios were closer to that of the entire bulk matrix than the Al/Fe mole ratio of colloids mobilized by phosphate treatment. We previously surmised that elevated pH induced mobilization by hydrolyzing bonds among amorphous iron oxyhydroxides and clay minerals while also generating repulsive interactions among matrix constituents by surpassing the pH_{pzc} of iron oxyhydroxides in the sediment [Swartz and Gschwend, 1998]. Note that dissolved Fe levels in BASE-9.59 were indistinguishable from levels observed in SDS2, PHOS, and the ambient groundwater, suggesting that dissolution of iron oxyhydroxides was not occurring (Figure 6). The in situ results support the hypothesis that hydrolysis may have allowed mobilization of colloids more representative of the bulk matrix upon contact of this sediment with elevated pH groundwater.

Under acidic conditions one would not expect mobilization of the goethite aggregates to occur if goethite-kaolinite face juxtapositions predominated in the matrix. Given these juxtapositions, the electrostatic interactions among these two constituents would be attractive at acidic pH. Amorphous iron oxyhydroxide-kaolinite face juxtapositions would be attractive as well. Although the breaking of bonds among the amorphous iron oxyhydroxides and the kaolinite would be expected to occur at low pH as proton-promoted dissolution of iron oxyhydroxides occurred [Zinder et al., 1986], the acidic pH would not impart the repulsive electrostatic conditions necessary to induce mobilization. Indeed, elevated levels of dissolved Fe, as compared to levels observed in PHOS, SDS2, and the ambient groundwater, were observed in the retrieved injectate of ACID (Figure 6), with no concomitant mobilization of colloids. This in situ behavior is in correspondence with the results from the packed-column studies, in which no turbidity was manifest when the sediment was treated with a 1 mM $CaCl_2$ pH 2.5 solution for up to 150 pore volumes [Swartz and Gschwend, 1998].

4.2. Transport of Mobilized Colloids

Colloid transport has recently been studied in packed-column systems [Saiers et al., 1994; Kretzschmar et al., 1997]. Using either a step or pulse input of a known concentration of synthetic colloids, the elution profiles of the colloids were analyzed with solutions for the advective-dispersive-reaction equation [Saiers et al., 1994; Kretzschmar et al., 1997]. The "reaction" term, reflecting colloid removal to the immobile

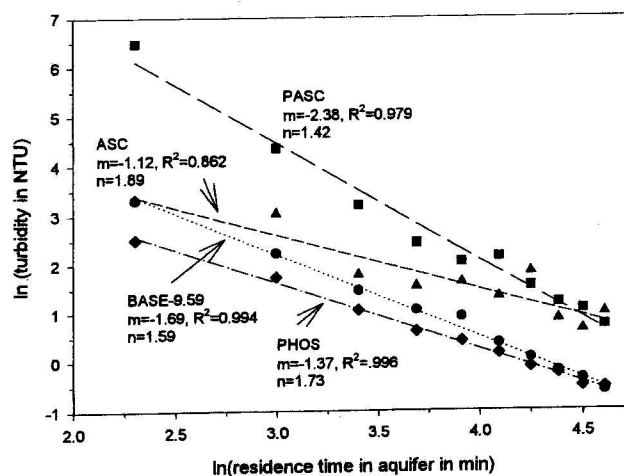


Figure 7. Linear regression of \ln (turbidity) versus \ln (residence time) to determine the reaction "order" of the transport of mobilized colloids in PHOS, ASC, PASC, and BASE-9.59. See Table 2 for the regression parameters obtained for the control experiments from these wells.

sediment, was best described by either first- or second-order behavior with respect to the aqueous phase colloid concentrations depending on whether repulsive or attractive electrostatic interactions, respectively, between colloids and collector surfaces prevailed [Saiers et al., 1994; Kretzschmar et al., 1997].

The colloid concentration data for the retrieved injectates in PHOS, ASC, BASE-9.59, and PASC, in which turbidity was elevated in comparison to the control levels, conformed well to (3). The values of the "reaction" order n (calculated from the regression slopes) for PHOS, ASC, PASC, and BASE-9.59 data fell between 1.0 and 2.0 (Figure 7). R^2 values for linear regression of \ln (turbidity) against \ln (contact time) for these experiments were 0.979 or higher (Figure 7), except for ASC, which had an R^2 value of only 0.862. Identical analysis using the data from each of the control experiments produced generally lower R^2 values (0.985 to 0.859, Table 2). The lower regression coefficients obtained for the control experiments may, in part, reflect the fewer elevated turbidity data points for these injectates, as turbidity typically fell to baseline values before dispersive mixing affected the samples in the control experiments.

For the control experiments the average value of n was 1.95 ± 0.33 (Table 2). The turbidity manifest in the discharge from these control experiments most likely resulted from the physical perturbation inherent in the injection-withdrawal pro-

Table 2. Colloid Transport Regression Parameters for Control Experiments

Experiment	Slope	n	R^2
BASE-BC2	-0.61	2.63	0.859
BASE-AC	-0.95	2.05	0.942
PASC-BC	-1.58	1.64	0.818
PASC-AC	-1.16	1.86	0.985
SDS-BC	-0.91	2.11	0.884
SDS-AC	-1.36	1.74	0.942
ACID-BC	-0.85	2.18	0.924
ASC-BC	-1.85	1.53	0.985
PHOS-BC	-1.25	1.80	0.906

cedure. It can be assumed that prevailing electrostatic interactions among matrix constituents were not altered by the injectate during these control experiments. The ambient electrostatic interactions among the matrix constituents would be expected to be attractive, as very low baseline turbidity levels in the groundwater indicated that the immobile matrix was stable. Thus the "loose" material mobilized in the control experiments would be expected to follow second-order transport behavior based on the work of *Saiers et al.* [1994]. Indeed, the average value of n (1.95 ± 0.33) for the control experiments is in agreement with these expectations. Note that the colloids and collectors in our field system consisted of the same phase, as the colloids are a mobilized subset of the collectors (the portion of the matrix which remains stationary).

In the experiments in which a mobilization event occurred, the value of n decreased systematically as the magnitude of the mobilization event increased (PHOS ($n = 1.73$) > BASE-9.59 ($n = 1.59$) > PASC ($n = 1.42$)). The data for ASC (Figure 4c) did not fit this trend, however. The highest value of n (1.89, Figure 7) was calculated for ASC even though the turbidity generated in this experiment was somewhat higher than either PHOS or BASE-9.59 (Compare Figures 4a, 4b, and 6b). Possible reasons for the behavior exhibited by ASC are discussed below.

The values for n for each of the mobilization experiments may provide an indication of the relative electrostatic repulsion generated by the different chemical amendments to the groundwater. For example, the values of n for PHOS (1.73) and ASC (1.89) were within 1 standard deviation of the average value of n for the control experiments. This suggests that electrostatic interactions among matrix constituents may not have been altered significantly by adding the 1 mM phosphate or 1 mM ascorbic acid to the groundwater. In contrast, the n values for data from BASE-9.59 and PASC were substantially lower (1.59 and 1.42, respectively) and closer to first order than the average n value for the control experiments. *Saiers et al.* [1994] and *Kretzschmar* [1997] found that a first-order reaction term better described colloid transport behavior when repulsive interactions prevailed between colloid and collector surfaces. Thus the lower values of n for BASE-9.59 and PASC suggest that the pH 9.59 groundwater and 0.5 mM phosphate to 0.5 mM ascorbate amended groundwater generated greater repulsive forces among mobilized colloids and collector surfaces (the matrix constituents that remained immobile). Note, however, that no electrophoretic mobility data for the mobilized colloids exist to support this interpretation.

Consideration of the Al/Fe mole ratios of the colloids generated by the different amendments may also aid in explaining the differences in n values among the experiments. Recall that analysis of the colloidal Al/Fe mole ratios of the injectates from BASE-9.59 and PASC suggested that these injectates mobilized colloids more representative of the entire bulk matrix (i.e., more clay minerals) than occurred in PHOS. Thus repulsive interactions between colloid and collector surfaces in BASE-9.59 and PASC may have been enhanced by the presence of a greater amount of clay minerals in the colloid phase in addition to probable greater negative charge of colloid and collector surfaces due to adsorption of amendment solutes.

It appears also that relatively more clay minerals were mobilized in ASC than were mobilized in PHOS (the Al/Fe mole ratios for ASC colloids and BASE-9.59 colloids were very similar, Table 1), even though the n value for the ASC experiment (1.89) was the highest of all four of the experiments. The

higher Al/Fe mole ratio of the ASC colloids would be expected based on the ability of ascorbic acid to break bonds among the amorphous iron oxyhydroxide-kaolinite assemblages as discussed in section 4.1. The higher value of n would be expected based on electrophoretic mobility studies which showed that pH 9 solutions imparted greater negative charge to model goethite colloids, for example, than even 10 mM ascorbic acid at pH 5.2 [*Swartz and Gschwend*, 1998]. The combined occurrence of relatively high values of turbidity and n in the ASC experiment does not fit the trend exhibited by the PHOS, BASE-9.59, and PASC data perhaps because of aggressive dissolution by the ascorbic acid (Figure 6). Matrix solids may have been "loosened" by the action of the ascorbic acid and, when combined with the physical perturbation inherent in the injection-withdrawal procedure, colloids were mobilized in greater amounts than would have occurred because of just the electrostatic repulsion imparted by ascorbic acid adsorption on matrix surfaces. Physical perturbation caused by the injection-withdrawal procedure may have caused greater turbidity to be manifest in all of the amendment injections than would have occurred because of electrostatic considerations alone. It may be that determination of the reaction order describing colloid transport of the mobilized colloids aided in distinguishing between physical and chemical perturbation in these cases.

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