

Final Report

Colloid-Facilitated Transport of Radioactive Cations in the Vadose Zone

1. Introduction

1.1. Objectives and Scope of the Research

The overarching goal of this study was to improve understanding of colloid-facilitated transport of radioactive cations through unsaturated soils and sediments. We conducted a suite of laboratory experiments and field experiments on the vadose-zone transport of colloids, organic matter, and associated contaminants of interest to the U.S. Department of Energy (DOE). The laboratory and field experiments, together with transport modeling, were designed to accomplish the following detailed objectives:

1. Evaluation of the relative importance of inorganic colloids and organic matter to the facilitation of radioactive cation transport in the vadose zone.
2. Assessment of the role of adsorption and desorption kinetics in the facilitated transport of radioactive cations in the vadose zone.
3. Examination of the effects of rainfall and infiltration dynamics and in the facilitated transport of radioactive cations through the vadose zone.
4. Exploration of the role of soil heterogeneity and preferential flow paths (e.g., macropores) on the facilitated transport of radioactive cations in the vadose zone.
5. Development of a mathematical model of facilitated transport of contaminants in the vadose zone that accurately incorporates pore-scale and column-scale processes with the practicality of predicting transport with readily available parameters.

This collaborative research project brought together scientists and engineers from Yale University, the University of Colorado, and Oak Ridge National Lab. This report focuses exclusively on findings based on laboratory experiments and model simulations carried out at Yale University. Findings from the field-scale transport experiment will be described separately in a final report submitted by the University of Colorado.

1.2. Relevance of Project to DOE Mission

The focus of this proposal on facilitated transport in the vadose zone directly addresses needs addressed by the U.S. Department of Energy for risk assessment and remediation of some of their contaminated sites (DOE-ERSD, 2006). In response to DOE needs outlined in the solicitation, the research described in this proposal will “investigate a key process affecting the mobility of subsurface contaminants found at DOE sites.” Because of the prevalence of radioactive cations and anions that strongly bind to mineral and organic matter phases at DOE sites, colloid- and organic matter-facilitated transport of contaminants has been examined and observed at DOE sites in both the vadose zone (Ryan *et al.*, 1998; Litaor *et al.*, 1998; McCarthy, 1998) and in saturated media (Buddemeier and Hunt, 1988; Kersting *et al.*, 1999; Santschi *et al.*, 2002; Dai *et al.*, 2005) and in laboratory experiments using partially saturated and saturated media from DOE sites (Coles and Ramspott, 1982; Um and Papelis, 2002; Flury *et al.*, 2002; Zhuang *et al.*, 2003; Chen *et al.*, 2005; Jackson *et al.*, 2005). Recent reviews also address the subject of the potential importance of colloids in the transport of contaminants at DOE sites (Triay *et al.*, 1995; Honeyman, 1999; Levi, 1999; Clark *et al.*, 2006), and efforts to model contaminant transport at DOE

sites also take facilitated transport into account (*Contardi et al.*, 2001; *Moridis et al.*, 2003; *Cvetkovic et al.*, 2004).

As requested by the DOE in the solicitation for this proposal, the objectives of this research are to “develop fundamental and quantitative understanding of the physical and chemical processes affecting contaminant transport in subsurface environments.” We expect that the results of this research will, as desired by the DOE, “provide scientific understanding that will allow DOE sites to incorporate coupled physical and chemical processes into decision-making for environmental remediation and long-term stewardship.” Improved understanding of facilitated transport of radioactive cations in the vadose zone will lead to more realistic assessments of the risks posed by contamination in surface soils at DOE sites. A major unknown in this assessment is the degree to which the vadose zone acts as a conduit for surface contaminants to reach groundwater. In groundwater, contaminants have the potential to move off DOE sites, and groundwater is a pathway of exposure leading to potential ingestion of contaminants in drinking water.

The research described in this proposal will allow us to meet another important DOE goal – to examine contaminant transport over a range of scales with the “ultimate goal of providing DOE with field-scale descriptions of subsurface processes affecting contaminant transport.” By following a progression from the pore scale to the column scale to the field scale, we will gain understanding of the fundamental processes and be able to evaluate the degree to which these fundamental processes should be incorporated in models of field-scale transport.

Our proposed research also focuses on key DOE contaminants – cesium-137 and strontium-90 – and their co-transport with colloids and organic matter. The choice of these contaminants is both responsive to DOE needs and valuable in testing a hypothesis concerning the importance of desorption kinetics in facilitated transport (*Turner et al.*, 2006). As requested by DOE, the research described in this proposal will focus on field experiments at a DOE facility, the Oak Ridge National Laboratory.

2. Background

2.1. Role of Mineral Colloids and Organic Matter in Contaminant Mobility

For nearly four decades, we have known that the transport of contaminants in saturated media is accelerated by the presence of mineral colloids and organic matter (OM) (*Champlin and Eichholz*, 1968; *Ballard*, 1971; *Vinten et al.*, 1983; *Champ et al.*, 1984; *Killey et al.*, 1984). These early experiments and field observations reported “facilitated” or “enhanced” contaminant transport in cases in which the contaminants were bound strongly by mobile colloids and OM (*McCarthy and Zachara*, 1989). Since McCarthy and Zachara’s review, further laboratory work has improved our understanding of the mechanisms and potential importance of colloid- and OM-facilitated transport in saturated porous media (*McCarthy and Zachara*, 1989; *Torok et al.*, 1990; *Dunnivant et al.*, 1992; *Puls and Powell*, 1992; *Saiers and Hornberger*, 1996a; *Sätmark et al.*, 1996; *Roy and Dzombak*, 1997; *Noell et al.*, 1998; *Saiers and Hornberger*, 1999; *Warwick et al.*, 2000; *Sen et al.*, 2002). In addition, further field investigations have shown that colloid- and OM-facilitated transport in the vadose zone and in groundwater is occurring at DOE sites (*Buddemeier and Hunt*, 1988; *Ryan et al.*, 1998; *McCarthy*, 1998; *McCarthy et al.*, 1998; *Kersting et al.*, 1999; *Roberts et al.*, 2004; *Dai*, 2005).

For colloid- and OM-facilitated transport to be important, contaminant binding to colloids and OM must be strong (i.e., high K_d) and slowly reversible relative to the time scale of transport (*McCarthy and Zachara*, 1989; *Vilks et al.*, 1993; *Roy and Dzombak*, 1998; *Bold et al.*, 2003; *Schmitt et al.*, 2003). The strength of contaminant binding by OM and adsorption by minerals

has been extensively investigated, but the kinetics of desorption has not always been emphasized. For evaluating the importance of facilitated transport, understanding the kinetics of desorption is essential. In addition, the effect of contaminant concentration on the strength of binding is only recently being investigated in detail (*Dzombak and Morel, 1990; Brown et al., 1999; Tipping, 2002.*). Because binding sites on colloids and in OM are typically heterogeneous, binding strength often decreases as the contaminant/sorbent ratio increases. For metal binding to OM, this is especially true – soft metals like mercury and silver bind very strongly to sulfur- and nitrogen-containing functional groups, and less strongly to the more abundant oxygen-containing functional groups (*Frenkel et al., 2000; Haitzer et al., 2002; Saada et al., 2003*). Finally, the presence of OM will affect the adsorption of contaminants to mineral colloids, resulting in the formation of ternary complexes. OM will generally enhance cation adsorption to minerals at lower pH values (*Dalang et al., 1984; Davis, 1984; Ho and Miller, 1985; Allard et al., 1989; Righetto et al., 1991; Düker et al., 1995; Murphy et al., 1999; Christl and Kretzschmar, 2001*). As pH increases, the adsorption of OM to minerals decreases and some cations, like uranyl and Pu(III,IV), may form anionic complexes; the result is that the presence of OM will decrease the adsorption of some metals and anions (*Nelson et al., 1985; Payne et al., 1996; Lenhart and Honeyman, 1999; Simeoni et al., 2003*).

The movement of contaminants that are bound to soil-water colloids and OM depends on the transport properties of these carriers. Colloids suspended within vadose-zone porewaters are susceptible to immobilization by depositional reactions that take place near solid-water and air-water interfaces. Studies on colloid deposition within unsaturated porous media have been conducted primarily in model systems, consisting of columns packed homogeneously with sand or soil (*DeNovio et al., 2004*). The results of these experiments reveal the general trend of increasing colloid deposition rates with decreasing volumetric moisture content (*Wan and Wilson, 1994a; Schäfer et al., 1998; Chu et al., 2001; Lenhart and Saiers, 2002; Cherrey et al., 2003*) and increasing porewater ionic strength (*Gamerding and Kaplan, 2001; Saiers and Lenhart, 2003a*). Results of visualization experiments with porous-medium micromodels indicate that this behavior reflects, in part, colloid adhesion at air-water interfaces (*Wan and Wilson, 1994b; Sirivithayapakorn and Keller, 2003; Keller and Sirivithayapakorn, 2004*). Colloid adhesion at air-water interfaces is sensitive to porewater chemistry and colloid surface composition and is governed by hydrophobic, capillary, and electrostatic forces (*Wan and Wilson, 1994b; Wan and Tokunaga, 1997; Sirivithayapakorn and Keller, 2003*). In addition to capture by air-water interfaces, colloids may be immobilized by straining, which occurs in pore throats that are too narrow to permit the colloids to pass (*Bradford et al., 2003*), within films of water that surround the mineral grains (*Wan and Tokunaga, 1997*), or at the air-water-solid contact within pendular rings of unsaturated pores (*Crist et al., 2004*). Colloid deposition also takes place at solid-water interfaces, and there is some evidence to suggest that the presence of the air phase increases the rate of this mass-transfer reaction (*Chu et al., 2001*).

The mobilization of deposited colloids is slow under steady flow, but transient-flow conditions that are typical of infiltration events drive rapid colloid release (*Kaplan et al., 1993; Ryan and Elimelech, 1996; Jacobsen et al., 1998; Saiers et al., 2003*). In the vadose zone, chemical perturbations (e.g., ionic strength reductions, pH increases) often occur concomitantly with flow transients and can promote mobilization by increasing repulsive forces between attached colloids and mineral grains (*Gamerding and Kaplan, 2001; Gao et al., 2004*). Chemical perturbations are not requisite to mobilization; however, as observations made under steady chemical conditions, but transient-flow conditions, suggest that changes in flow alone can drive rapid colloid release (*Saiers and Lenhart, 2003b*). Colloid mobilization during transient flow likely reflects interactions between multiple mechanisms. The increase in shear stress on attached colloids that arises from flow-rate increases during infiltration may induce

mobilization (Kaplan *et al.*, 1993; Lægdsmand *et al.*, 1999; Weisbrod *et al.*, 2002). Moving air-water interfaces, in addition to high flow rates, are a characteristic feature of transient-flow regimes. Some researchers have proposed that mobile interfaces may scour colloids from the surfaces of mineral grains and facilitate their downward transport through the soil (El-Farhan *et al.*, 2000; Sayers *et al.*, 2003). Changes in air-water configuration that take place during porous-medium imbibition also contribute to mobilization. For example, colloids strained by thin-water films that line partially saturated pores are mobilized as these films expand upon porous-medium imbibition (Gao *et al.*, 2006).

Compared to the number of studies that have explored deposition and mobilization of mineral colloids, fewer studies have examined OM transport (Dunnivant *et al.*, 1992; Jardine *et al.*, 1992; Johnson and Amy, 1995; Johnson *et al.*, 2002; Lenhart and Sayers, 2004), and only one of these has been conducted in unsaturated porous media (Lenhart and Sayers, 2004). Results of this study demonstrated that sorptive reactions at air-water interfaces reduced OM mobility and that the affinity of OM for the air phase increased as the porewater pH declined. Desorption of OM from the air-water interfaces was found to be negligible for conditions of steady porewater flow and chemistry, but substantial release of bound OM occurred in response to pH perturbations (Lenhart and Sayers, 2004).

Mathematical models that account for the co-transport of contaminants by colloids and OM have been developed (Corapcioglu and Jiang, 1993; Sayers and Hornberger, 1996b; Roy and Dzombak, 1998). These models solve equations that describe contaminant partitioning between the aqueous, colloidal, and stationary phases in coordination with equations that describe contaminant transport in the aqueous and colloidal phases (Figure 1). Comparisons of calculations from these models to data collected from laboratory column experiments conducted with clean quartz sand and under water-saturated conditions suggest that these models are appropriate for approximating facilitated transport under idealized conditions (Sayers and Hornberger, 1996a; Sayers and Hornberger, 1999; Turner *et al.*, 2006). No attempts, however, have been made to evaluate models against data collected from experiments conducted with real soils under variably saturated conditions.

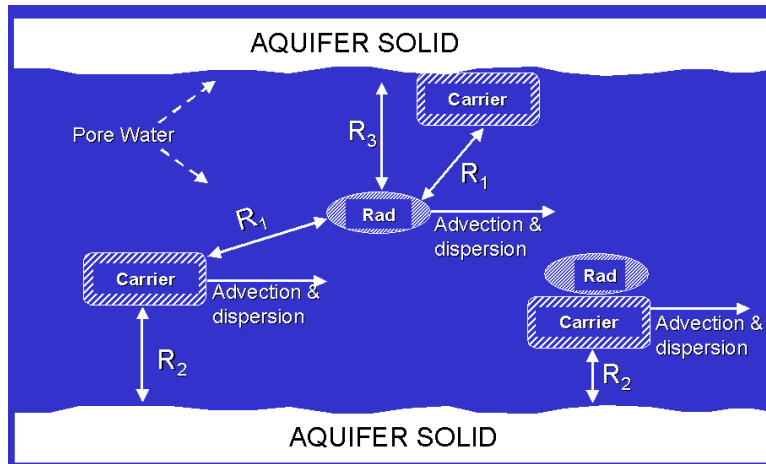


Figure 1. Transport processes and mass-transfer reactions (denoted by R_1 , R_2 , and R_3) considered in published models for the co-transport of radionuclides (Rad) by organic matter or mineral-colloid carriers.

3. Project Findings

3.1 Colloid-Facilitated Transport of Cesium during Transient Flow

3.1.1 Overview Experimental Methods

We measured the mobilization of *in situ* (not injected) colloids and ^{137}Cs from ^{137}Cs -contaminated sediments during porous-medium drainage and imbibition. Hanford Coarse Sand (HCS) was selected as the porous medium for these experiments because it has been previously characterized and used in published experiments on colloid transport.

Separate sets of duplicate experiments were conducted at pore water ionic strengths that spanned from 0.16 mM to 50 mM and that fall within the range of ionic strengths reported for natural soil waters. Although the experiments were characterized by periods of transient pore water flow, pore water ionic strength was held constant throughout the duration of each experiment. Experiments at an ionic strength of 2 mM were conducted in columns of two different lengths (20.8 and 10.4 cm) to evaluate the effects of colloid re-deposition on the quantities of colloids and ^{137}Cs delivered through the sand packs.

All experiments were conducted in an acrylic column measuring 5 cm in diameter (Figure 2). A 20 μm pore-size nylon membrane was used at the bottom of the column to maintain capillary pressure in the column. Peristaltic pumps, connected to the top and bottom of the column, regulated the downward flow of water through the sand-pack. The effluent was collected with a fraction collector, located beyond the column outlet. Pressure head in the column was measured by tensiometers installed at 5.2, 10.4, and 15.6 cm from the top of the column. The tensiometers were connected to a data-logger to provide a continuous record of pressure head throughout the experiments.

For each experiment, a column was packed by pouring the water-saturated, ^{137}Cs pre-equilibrated (contaminated) HCS in ~ 35 g increments into the column. After each increment of sand, the contents of the column were stirred using a stainless-steel rod and the sides of the column were tapped to mix the sand and remove air bubbles. The column was packed to a bulk density of 1.59 g cm^{-3} , which, assuming an average particle density of 2.65 g cm^{-3} for the quartz-dominated sediment, corresponds to porosity of 0.40. Most columns were packed to a height of 20.8 cm with 650 g of HCS; one set of columns was packed to a height of 10.4 cm with 325 g of HCS.

Mobilization of *in situ* (not injected) colloids and ^{137}Cs was measured during both drainage and imbibition of the sand columns. In the first phase of the experiments, a column containing Cs-contaminated HCS was flushed for three pore volumes under water-saturated conditions with colloid- and Cs-free artificial pore water by setting the specific discharge at the top (q_{top}) and bottom (q_{bot}) of the column equal to 0.23 cm min^{-1} . Sand-pack drainage was initiated after the column flush by a step-change reduction in q_{top} from 0.23 to 0.08 cm min^{-1} . The downward propagating drying front promoted the release of *in situ* colloids from the HCS, which were detected by continuous sampling of the column effluent. Once the drying front reached the column bottom, q_{bot} and q_{top} were set equal to 0.08 cm min^{-1} , which led to the re-establishment of steady flow within the sand pack and a decline in effluent colloid concentrations. After the colloid concentrations stabilized at low levels, sand-pack imbibition was initiated by increasing q_{top} from 0.08 to 0.25 cm min^{-1} , while holding q_{bot} constant at 0.08 cm min^{-1} . Once the wetting front reached the column bottom, q_{bot} and q_{top} were equalized at 0.25 cm min^{-1} and steady flow was re-established within the sand pack.

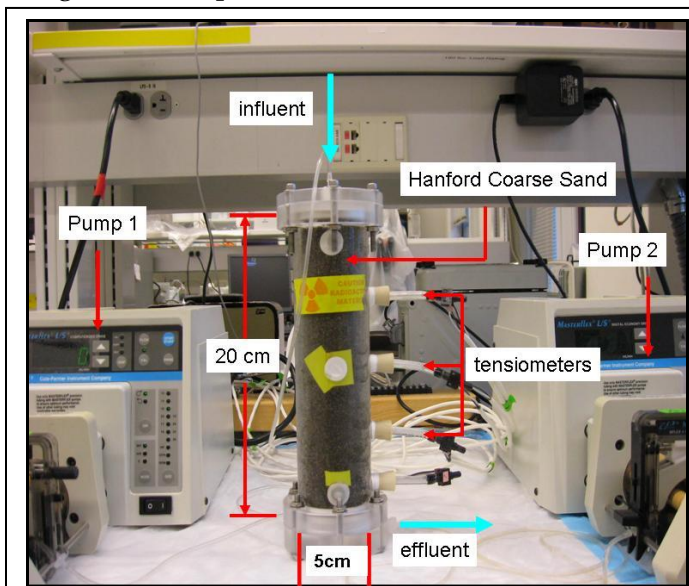


Figure 2. Laboratory column used in transport

3.1.2 Results and Discussion

Transient pore water flow. Sand-pack drainage was initiated by lowering the specific discharge at the top of the column by a factor of three, while holding the specific discharge at the base of the column constant (Figure 3A, 3B). The pressure head (Ψ), measured at three locations (one location for the 10.4 cm column) along the column, declined from positive values to -32 cm as the drying front moved downward through the column (Figure 3C, 3D). Calculations based on the water-retention characteristics of the HCS indicate that the measured decrease in Ψ corresponded to a decline in volumetric moisture content (Θ) from 0.4 to 0.22 (Figure 3E, 3F). The drying front reached the base of the column in 25 and 12 minutes for the 20.8 and 10.4 cm columns, respectively, whereupon q_{top} and q_{bot} were set equal to 0.08 cm min^{-1} to establish steady flow ($\partial\Theta/\partial t = \partial\Psi/\partial t = 0$) and nearly uniform Ψ and Θ .

Sand-pack imbibition was initiated following the steady-flow period by increasing q_{top} to 0.25 cm min^{-1} (Figure 3A, 3B). The wetting front moved rapidly through the column, as indicated by the step-like increases in Ψ (Figure 3C, 3D), and reached the column bottom in 4-8 minutes (depending upon column length). Once the wetting front reached the column base, inflow and outflow rates were equalized, leading to a period of steady flow in which Ψ exhibited small spatial variability and had a depth-averaged value of -18 cm. The volumetric moisture content (Θ) increased from 0.22 to 0.29 during the imbibition event.

Colloid mobilization and transport. During each drainage/imbibition event, effluent colloid concentrations increased from near-zero to peak values shortly after the passage of the drying/wetting front, then rapidly decreased to near-zero after the re-establishment of steady flow in the column (Figure 4). This pulse-type colloid release demonstrates that changes in volumetric moisture content and associated changes in pore scale, air-water interface configuration result in rapid colloid mobilization. Scouring by moving air-water interfaces presumably controls colloid mobilization during drainage, while thin-film expansion, reconnection of stagnant-water zones with bulk-water flow, and, perhaps, increases in shear forces contribute to colloid mobilization during imbibition. At least under the experimental conditions examined in this study, porous-medium drainage mobilized a greater mass of colloids than porous-medium imbibition; however, this relationship may depend on the sequence of wetting and drying events. Our analysis of SEM images of colloids eluted from a HCS column and retained on a $0.2 \text{ }\mu\text{m}$ filter membrane indicated that roughly 36%, 27%, 18%, and 18% of the colloids ranged from 0.2 to 0.5, 0.5 to 1.0, 1.0 to 1.5, and 1.5 to $2.0 \text{ }\mu\text{m}$, respectively.

Release of *in situ* colloids during transient flow was influenced by pore water ionic strength (Figure 4). As ionic strength increased from 0.16 to 50 mM, the peak effluent colloid concentrations during drainage and imbibition decreased 24-fold (from 1608 to 66 mg/L) and 34-fold (from 341 to 10 mg/L), respectively, and the total mass of colloids eluted during drainage and imbibition decreased 51-fold from 77 to 1.5 mg. These relationships may reflect that repulsive double-layer forces between colloids and the porous media are lower at high ionic strength and hence sand-bound colloids are less susceptible to detachment. Although colloid mobilization declined precipitously with increasing ionic strength in the transient flow experiments, peak colloid concentrations exceeded 60 mg/L, even at the highest ionic strength tested (50 mM).

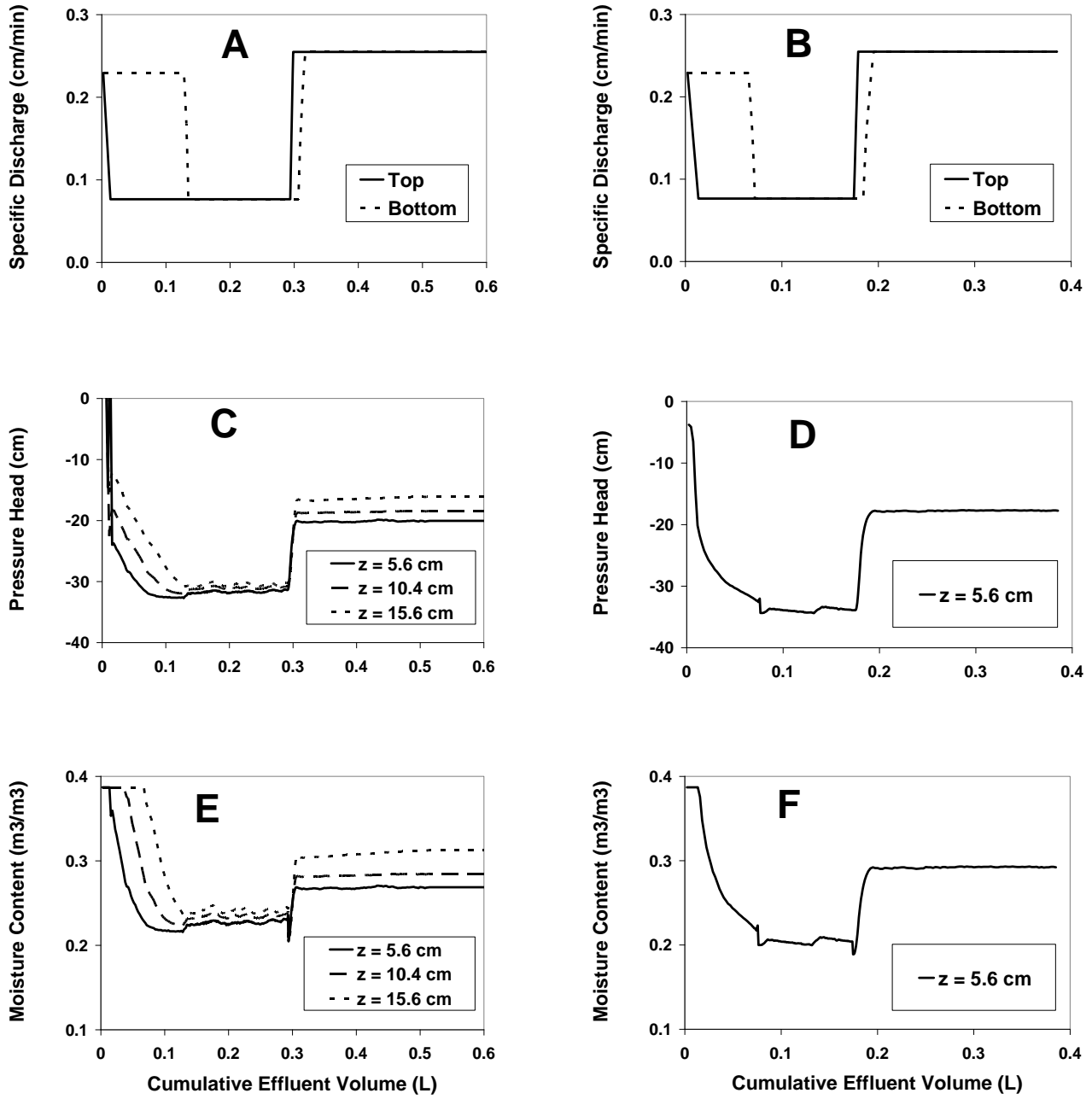


Figure 3. Measurements and calculations of (A) – (B) specific discharge at the top (q_{top}) and bottom (q_{bot}) of the sand column; (C) – (D) pressure head (Ψ) at three locations (one location for the 10.4 cm column) measured from the top of the column; and (E) – (F) volumetric moisture content (Θ) at three locations (one location for the 10.4 cm column) measured from the top of the column. (A), (C), and (E) are representative data sets for treatments 1-3 ($L = 20.8$ cm); (B), (D), and (F) are representative data sets for treatment 4 ($L = 10.4$ cm).

Cs mobilization and transport. Transient-flow conditions associated with sand-pack drainage and imbibition promoted Cs release from the HCS (Figure 4). During drainage and imbibition, Cs breakthrough characteristics mimicked those of the *in situ* colloids that were mobilized from the HCS. That is, effluent Cs concentrations peaked nearly synchronously with the passage of the wetting/drying front and declined towards zero as flow stabilized. In each treatment, effluent Cs concentrations were correlated with colloid concentrations, suggesting a strong linkage between Cs and colloid transport.

Measurements of the total, dissolved, and colloid-associated Cs concentrations reveal that Cs occurred predominantly in the dissolved phase when effluent colloid concentrations were low, and the proportion of Cs present in the colloidal phase increased with colloid concentrations. At $I = 2$ mM, for example, 94% of effluent Cs was present in the dissolved phase during the steady-flow period between drainage and imbibition events when effluent colloid concentrations were less than 2 mg/L, but more than 94% and 86% of Cs was colloid bound when colloid concentrations peaked at 1050 and 120 mg/L during drainage and imbibition, respectively. Similarly, greater than 99% of Cs existed in the dissolved form when effluent colloid concentrations were below 0.6 mg/L in the 50 mM experiments during the steady-flow period that separated the drainage and imbibition events. However, the colloidal form accounted for more than half the mobile Cs when effluent colloid concentrations peaked during drainage and imbibition. These observations demonstrate the colloid effect on Cs mobility can be substantial during transient flow, when high concentrations of colloids are mobilized.

Like colloid release, Cs mobilization during transient flow was sensitive to changes in pore water ionic strength. As ionic strength increased from 0.16 to 50 mM, peak Cs concentrations during drainage and imbibition decreased 15-fold and 4.5-fold, respectively, and the total mass of Cs eluted during drainage and imbibition decreased 3-fold (Figure 4). The decline in Cs transport with increasing ionic strength reflects the influences of ionic strength on colloid mobility and on the partitioning of Cs between the colloidal and aqueous phases. At ionic strength of 0.16 mM, colloid concentrations exceeded 1.5 g/L in some effluent samples (Figure 2), and these colloids carried substantial quantities of Cs, thereby shielding the contaminant from adsorption to the HCS. Much lower concentrations of colloids were mobilized in experiments at an ionic strength of 50 mM, where peak effluent concentrations associated with drainage and imbibition were an order of magnitude less than those at $I = 0.16$ mM. Furthermore, K_{ave} was five-fold less at $I = 50$ mM (relative to 0.16 mM) owing to increased competition from Na ions for ion-exchange sites on the colloids. Thus, decreases in the suspended load combined with decreases in the affinity of Cs for the colloidal phase accounted for the observed decline in Cs mobilization with increasing ionic strength.

The total mass of colloid-associated Cs eluted in the transient-flow experiments did not exceed 0.3% of the initial mass of Cs present with the HCS columns. Although the fraction of Cs mobilized was small, it is not trivial considering that our experiments mimicked only a single infiltration (wetting/drying) event. Based on an initial concentration of colloids available for mobilization from the HCS of 0.54 ± 0.02 mg g⁻¹ (obtained from batch-extraction measurements), and a HCS mass of 650 g, we estimate that repeated imbibition and drainage events could mobilize $0.54 \times 650 = 350$ mg of colloids from our 20-cm HCS column. Using this

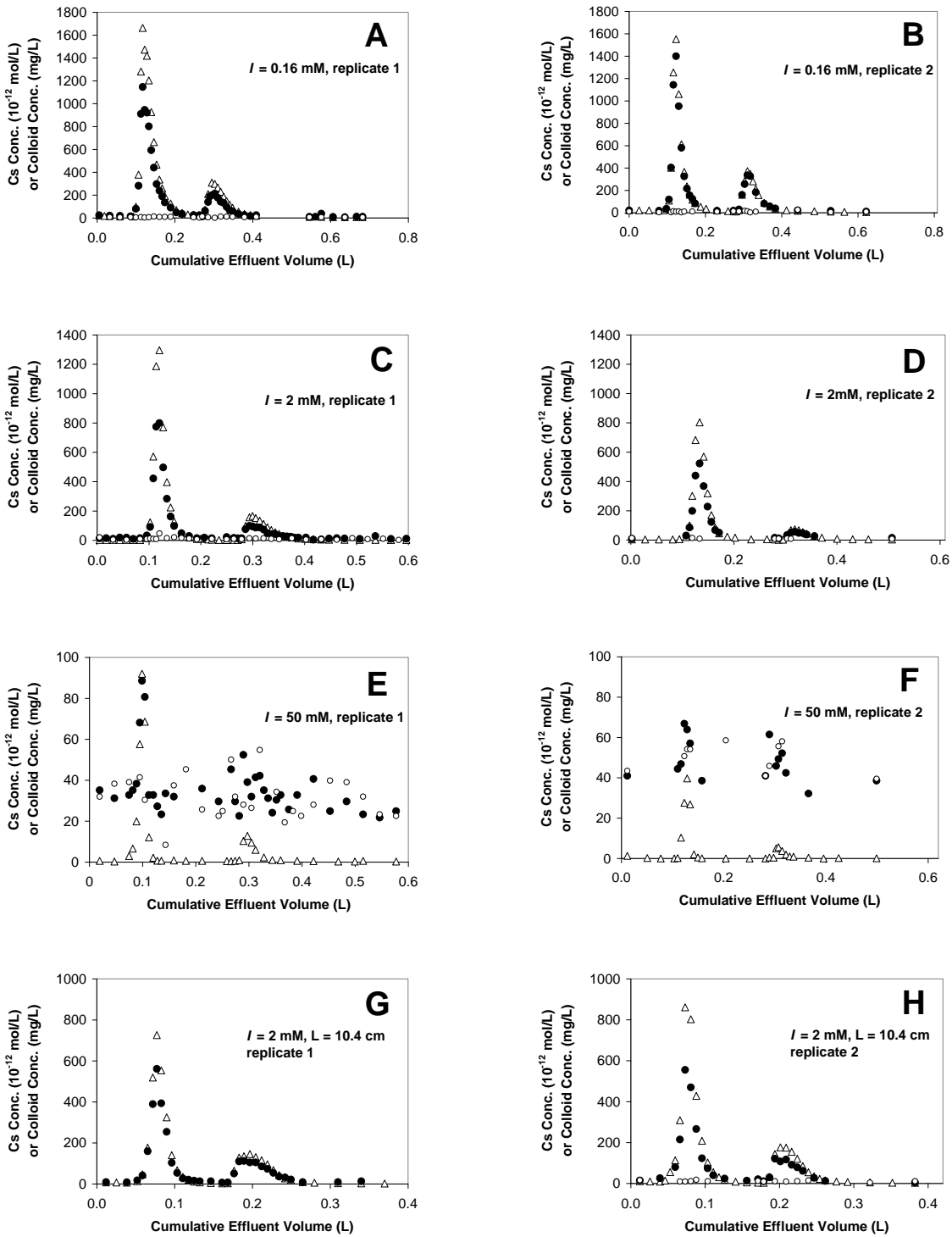


Figure 4. *In situ* colloid and Cs release from Cs-contaminated HCS during drainage and imbibition. The symbols represent experimentally measured effluent concentrations of colloids (Δ), total Cs (\bullet), and dissolved Cs (\circ). A and B: treatment 1 ($I = 0.16$ mM); C and D: treatment 2 ($I = 2$ mM); E and F: treatment 3 ($I = 50$ mM); G and H: treatment 4 ($I = 0.16$ mM, $L = 10.4$ cm).

value in coordination with the average concentration of Cs adsorbed to the colloids at $I = 0.16$ mM, we estimate that 1.2% of the Cs present within the HCS column was associated with colloids and could be mobilized through repeated drainage and imbibition events. This estimate, however, may be conservative because it is based on the assumption that the colloid supply is finite and will become depleted. Over environmentally relevant time scales that exceed those evaluated in our experiments, soil-weathering processes, as well as secondary-mineral formation, generate new colloid-sized particles that become eligible for mobilization. Colloid-facilitated transport could thus be a persistent phenomenon as colloids are continuously formed by physical, chemical and biological processes and mobilized by flow transients.

Effects of colloid re-deposition on transport. During drainage, the quantities of colloids and Cs released increased as the column length increased from 10.4 cm to 20.8 cm. Because the mass of *in situ* colloids available for mobilization varies proportionately with column length, a two-fold increase in column length should have doubled the mass of colloids eluted from the columns, provided that the mobilized colloids traveled conservatively. In our experiments, an increase in column length from 10.4 to 20.8 cm led to a 45% increase in colloid mass eluted and a 55% increase in Cs mass eluted during drainage, which is approximately half the amount expected if the mobilized colloids traveled conservatively. These results, then, reveal that colloids mobilized by porous-medium drainage are susceptible to re-deposition even while pore water flow continues. The opposite trend was observed during porous-medium imbibition. That is, for the same increase in column length (10.4 to 20.8 cm), the quantity of colloid eluted decreased 14% from 8.0 to 6.9 mg, and the quantity of colloid-associated Cs eluted decreased 24% from 51×10^{-13} to 39×10^{-13} mol. We cannot definitively account for this imbibition response, but the relationship is consistent with the notion that colloids mobilized by downward propagating wetting fronts traveled only a short distance before re-depositing and that re-distribution of the colloids and Cs during the preceding drainage event led to a greater accumulation of colloids and Cs at the base of the shorter (10.4 cm) columns that were eligible for mobilization once porous-medium imbibition was initiated. In water-unsaturated porous media, colloid deposition is influenced by processes associated with the air phase (e.g., film straining, air-water interface capture), in addition to attachment to solid-water interfaces. These air-phase associated mechanisms may explain the significance of colloid re-deposition in our partially water-saturated experiments and in other partially saturated systems even at low ionic strengths.

Environmental implications. This study demonstrates that porous-medium drainage and imbibition promote the release of *in situ* colloids and colloid-associated contaminants. Therefore, it is expected that colloid-facilitated transport in the vadose zone will be especially important during periods of transient flow that are induced, for example, by rainfall, snowmelt, and irrigation. The importance of *in situ* colloids as agents of Cs transport was influenced strongly by ionic strength of the infiltrating water. Our results suggest that high salt concentrations suppress colloid mobilization, increase colloid deposition, and lower Cs adsorption to colloids and thus diminish the colloid effect on Cs mobility. This is consistent with observations made at the Hanford site, where Cs movement through the vadose zone is controlled by dissolved-phase transport following the leakage of liquid wastes from storage tanks that contain high concentrations of salt and Cs. Nevertheless, our findings do suggest that in less saline vadose-zone environments or for contaminants with sorptive affinities that are less sensitive to ionic strength, the role of colloids in regulating contaminant fluxes through unsaturated soils should be considered.

3.2 Influence of Dissolved Natural Organic Matter on Colloid-Facilitated Transport of Cs-137

Another aspect of our laboratory-based research involved elucidating the effects of dissolved organic carbon (DOC) on the colloid-facilitated transport of radionuclides through porous media. DOC is ubiquitous in soil waters and groundwaters, and it binds to mineral colloids, as well as to soils and sediments. Moreover, DOC is capable of influencing the mobility of mineral colloids, as well as the manner in which these colloids adsorb and co-transport dissolved contaminants.

To improve understanding of the role of DOC in governing radionuclide mobility within geologic environments, we conducted a suite of column experiments on the migration of Cs through a porous medium. The experiments were distinguished on the basis of water-saturation, porous-medium composition, and composition of the influent suspension, which contained Cs only or Cs plus some combination of DOC, illite colloids, and kaolinite colloids (Table 1).

Table 1. Experimental treatments

Experiment ID	Water saturation	Porous medium	Injected species	Colloid type	Colloid conc. (mg/L)	DOC conc. (mg/L)
C1	unsaturated	quartz sand	Cs			
C2	unsaturated	quartz sand	Cs +DOC			5
C3	unsaturated	HCS	Cs			
C4	unsaturated	HCS	Cs +DOC			5
C5	unsaturated	quartz sand	Cs + illite	illite	100	
C6	unsaturated	quartz sand	Cs + illite +DOC	illite	100	5
C7	unsaturated	HCS	Cs + illite	illite	100	
C8	unsaturated	HCS	Cs + illite + DOC	illite	100	5
C9	unsaturated	HCS	Cs + kaolinite	kaolinite	100	
C10	unsaturated	HCS	Cs + kaolinite +DOC	kaolinite	100	5
C11	saturated	HCS	Cs + illite	illite	100	
C12	saturated	HCS	Cs + illite + DOC	illite	100	5

Results of the experiments demonstrate that Cs mobility was negligible in experiments conducted in the absence of illite and kaolinite colloids, even in experiments in which DOC was co-injected with the Cs. These results suggest that dissolved Cs had a strong affinity for the porous medium and that the DOC used in this study had little capacity to bind Cs. The addition of kaolinite colloids and illite colloids increased the mobility of Cs, and Cs detected in the column effluent in these experiments was almost entirely in the colloid-associated form. In experiments in which DOC was added to the column influent, the mobility of both mineral colloids and Cs substantially increased (Figures 5 and 6). Comparison of Figures 5 and 6 demonstrate that Cs transport was enhanced to a greater degree by illite colloids than by kaolinite colloids, regardless of the presence or absence of DOC.

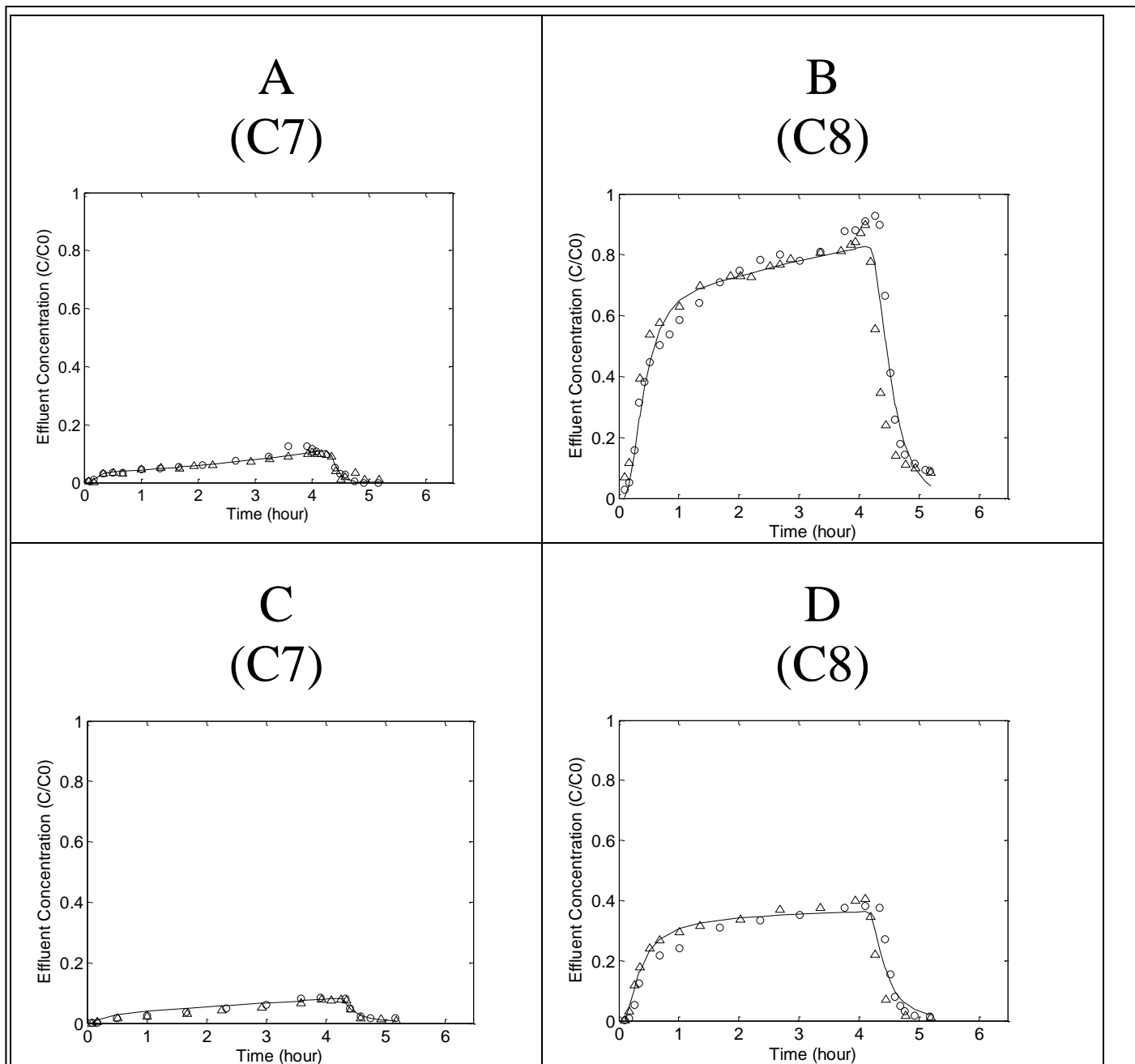
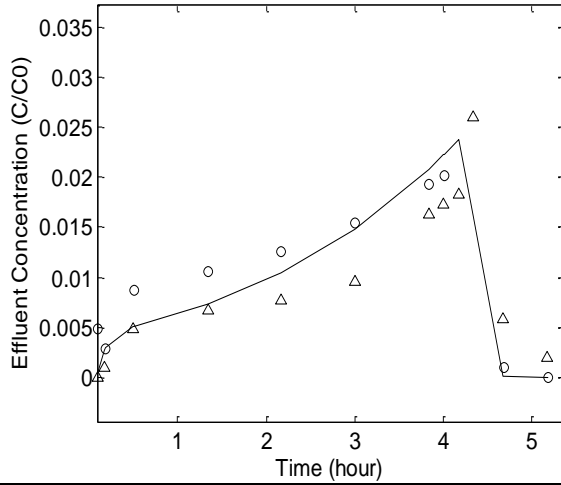


Figure 5. Measured (symbols) and modeled (lines) breakthrough curves for illite colloids and Cs. Panels A and B depict effluent illite concentrations for treatments without DOC and with DOC, respectively, and panels C and D reflect corresponding effluent Cs concentrations. The alphanumeric sub-titles that appear in parentheses refer to the treatment descriptions given in Table 1.

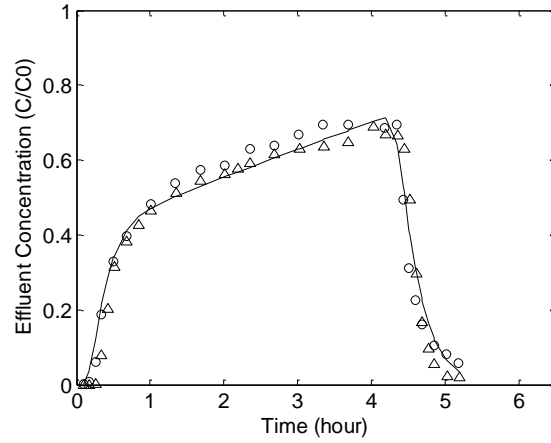
A mathematical model was applied to the column data to quantify the manner in which DOC affects colloid-sand, Cs-sand, and Cs-colloid interactions. This model accounted for several mass transport and rate-limited mass transfer processes, including the advective-dispersive transport of colloids, dissolved, Cs, and colloid-bound Cs; (ii) rate-limited colloid deposition onto the sand grains, and (iii) rate-limited Cs adsorption to suspended mineral colloids and the sand grains. This model successfully reproduced the breakthrough curves of Cs and mineral colloids (see Figure 5 and 6). Analysis of the modeling results demonstrates that DOC reduced deposition rates of illite and kaolinite by more than an order of magnitude, but had more moderate effects on the kinetics of Cs interactions with the mineral colloids and sand grains.

The findings from this research reveal the importance of DOC in influencing the movement of radionuclides in geologic environments that contain mobile colloids. Our research also advances a modeling approach that can serve as a framework for quantitative descriptions of this phenomenon.

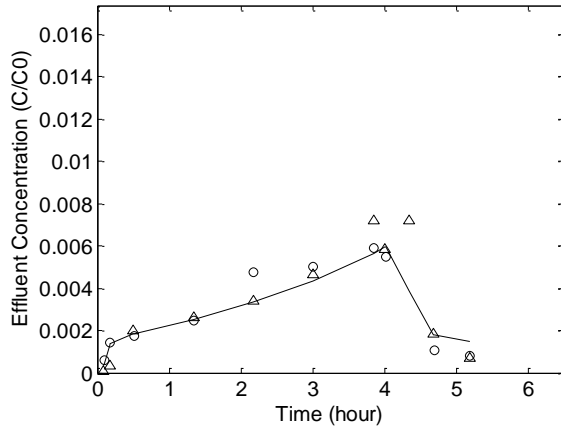
A
(C9)



B
(C10)



C
(C9)



D
(C10)

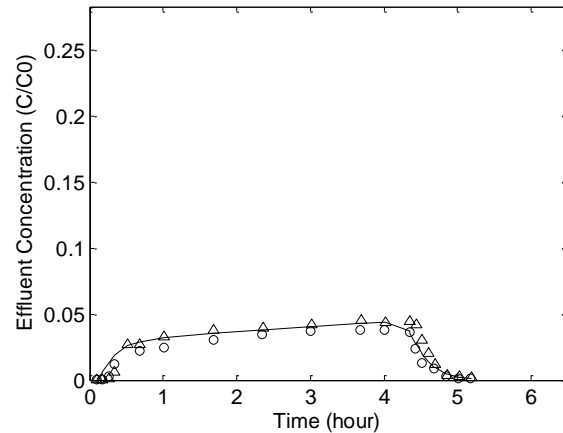


Figure 6. Measured (symbols) and modeled (lines) breakthrough curves for kaolinite colloids and Cs. Panels A and B depict effluent kaolinite concentrations for treatments without DOC and with DOC, respectively, and panels C and D reflect corresponding effluent Cs concentrations. The alphanumeric sub-titles that appear in parentheses refer to the treatment descriptions given in Table 1.

REFERENCES

- Allard, B., Moulin, V., Basso, L., Tran, M.T. and Stammose, D., 1989. Americium adsorption on alumina in the presence of humic materials. *Geoderma*, 44: 181-187.
- Arnseth, R. W. and Turner, R. S., 1988. Sequential extraction of iron, manganese, aluminum, and silicon in soils from two contrasting watersheds. *Soil Science Society of America Journal*, 52: 1801-1807.
- Ballard, T.M., 1971. Role of humic carrier substances in DDT movement through forest soil. *Soil Science Society of America Journal*, 35: 145-147.
- Bold, S., Kraft, S., Grathwohl, P. and Liedl, R., 2003. Sorption/desorption kinetics of contaminants on mobile particles: Modeling and experimental evidence. *Water Resources Research*, 39: doi:10.1029/2002WR001798.
- Bradford, S.A., Simunek, J., Bettahar, M., Van Genuchten, M.T. and Yates, S.R., 2003. Modeling colloid attachment, straining, and exclusion in saturated porous media. *Environmental Science & Technology*, 37(10): 2242-2250.
- Brown, G.E.J., Henrich, V.E., Casey, W.H., Clark, D.L., Eggleston, C., Felmy, A., Goodman, D.W., Gratzel, M., Maciel, G., McCarthy, M.I., Nealson, K.H., Sverjensky, D.A., Toney, M.F. and Zachara, J.M., 1999. Metal oxide surfaces and their interactions with aqueous solutions and microbial organisms. *Chemical Reviews*, 99: 77-174.
- Bruque, S., Mozas, T. and Rodriguez, A., 1980. Factors influencing the retention of lanthanide ions by montmorillonite. *Clay Minerals*, 15: 413-420.
- Buddemeier, R.W. and Hunt, J.R., 1988. Transport of colloidal contaminants in groundwater: Radionuclide migration at the Nevada Test Site. *Applied Geochemistry*, 3: 535-548.
- Champ, D.R., Young, J.L., Robertson, D.E. and Abel, K.H., 1984. Chemical speciation of long-lived radionuclides in a shallow groundwater flow system. *Water Pollution Research Journal of Canada*, 19: 35-54.
- Champlin, J.B.F. and Eichholz, G.G., 1968. The movement of radioactive sodium and ruthenium through a simulated aquifer. *Water Resources Research*, 4: 147-158.
- Chen, G. and Flury, M., 2005. Retention of mineral colloids in unsaturated porous media as related to their surface properties. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 256: 207-216.
- Cherrey, K., Flury, M. and Harsh, J., 2003. Nitrate and colloid transport through coarse Hanford sediments under steady state, variably saturated flow. *Water Resources Research*, 39: 1165, doi: 10.1029/2002WR001944.
- Christl, I. and Kretzschmar, R., 2001. Interaction of copper and fulvic acid at the hematite-water interface. *Geochimica et Cosmochimica Acta*, 65: 3435-3442.
- Chu, Y., Jin, Y., Flury, M. and Yates, M., 2001. Mechanisms of virus removal during transport in unsaturated porous media. *Water Resources Research*, 37(2): 253-263.
- Clark, D. L., Janecky, D. R. and Lane, L. J., 2006, Science-based cleanup of Rocky Flats. *Physics Today*, 59(9): 34-40.
- Coles, D. G. and Ramspott, L. D., 1982. Migration of ruthenium-106 in a Nevada Test Site aquifer: discrepancy between field and laboratory results. *Science*, 215: 1235-1237.
- Contardi, J. S., Turner, D. R. and Ahn, T. M., 2001. Modeling colloid transport for performance assessment. *Journal of Contaminant Hydrology*, 47: 323-333.
- Corapcioglu, M.Y. and Jiang, S., 1993. Colloid facilitated groundwater contaminant transport. *Water Resources Research*, 29: 2215-2216.
- Crist, J.T., McCarthy, J.F., Zevi, Y., Baveye, P., Throop, J.A. and Steenhuis, T.S., 2004. Pore-scale visualization of colloids transport and retention in partly saturated porous media. *Vadose Zone Journal*, 3: 444-450.

- Crist, J.T., Zevi, Y., McCarthy, J.F., Troop, J. and Steenhuis, T.S., 2005. Transport and retention of colloids within partially saturated porous media. *Vadose Zone Journal*, 4: 184-195.
- Cvetkovic, V., Painter, S., Turner, D., Pickett, D. and Bertetti, P., 2004. Parameter and model sensitivities for colloid-facilitated radionuclide transport on the field scale, *Water Resources Research*, 40: W06504-doi:10.1029/2004WR003048.
- Dai, M., Buesseler, K. O. and Pike, S. M., 2005. Plutonium in groundwater at the 100K-Area of the U.S. DOE Hanford site. *Journal of Contaminant Hydrology*, 76: 167-189.
- Dalang, F., Buffle, J. and Haerdi, W., 1984. Study of the influence of fulvic substances on the adsorption of copper(II) ions at the kaolinite surface. *Environmental Science & Technology*, 18: 135-141.
- Davis, J.A., 1984. Complexation of trace metals by adsorbed natural organic matter. *Geochimica et Cosmochimica Acta*, 48: 679-691.
- DeNovio, N.M. and Ryan, J.N., in review. Using particle size to evaluate particle mobilization mechanisms in unsaturated sand columns during simulated rainfall. *Environmental Science & Technology*.
- DeNovio, N.M., Ryan, J.N., Saiers, J.E. and Ranville, J.F., in preparation. Mobilization of metals associated with colloids and organic matter by simulated rainfall in intact cores of a metal-contaminated soil. *Environmental Science & Technology*.
- DeNovio, N.M., Saiers, J.E. and Ryan, J.N., 2004. Colloid movement in unsaturated porous media: Recent advances and future directions. *Vadose Zone Journal*, 3: 338-351.
- Dittrich, T., Ryan, J.N., and Saiers, J.E., in preparation. Facilitated transport of cesium and strontium on illite colloids through homogeneous unsaturated porous media.
- Dittrich, T., Ryan, J.N., and Saiers, J.E., in preparation. Facilitated transport of cesium and strontium on illite colloids through physically heterogeneous unsaturated porous media.
- DOE-ERSD, 2006. Environmental Remediation Sciences Program Strategic Plan, draft, version 0.9; accessed April 1, 2007, at http://www.sc.doe.gov/ober/ERSD/ERSD_2006_Strategic_Plan.pdf.
- Düker, A., Ledin, A., Karlsson, S. and Allard, B., 1995. Adsorption of zinc on colloidal (hydr)oxides of Si, Al and Fe in the presence of fulvic acid. *Applied Geochemistry*, 10: 197-205.
- Dunnivant, F.M., Jardine, P.M., Taylor, D.L. and McCarthy, J., 1992. Cotransport of cadmium and hexachlorobiphenyl by dissolved organic carbon through a column containing aquifer material. *Environmental Science & Technology*, 26: 360-368.
- Dzombak, D.A. and Morel, F.M.M., 1990. *Surface Complexation Modeling: Hydrous Ferric Oxide*. John Wiley & Sons, New York.
- El-Farhan, Y.H., DeNovio, N.M., Herman, J.S. and Hornberger, G.M., 2000. Mobilization and transport of soil particles during infiltration experiments in an agricultural field, Shenandoah Valley, Virginia. *Environmental Science & Technology*, 34: 3555-3559.
- Flury, M., Mathison, J. B. and Harsh, J. B., 2002. In situ mobilization of colloids and transport of cesium in Hanford sediments. *Environmental Science & Technology*, 36: 5335-5341.
- Frenkel, A.I., Korshin, G.V. and Ankudinov, A.L., 2000. XANES study of Cu²⁺-binding sites in aquatic humic substances. *Environmental Science & Technology*, 34: 2138-2142.
- Gamerding, A.P. and Kaplan, D.I., 2001. Physical and chemical determinants of colloid transport and deposition in water-unsaturated sand and Yucca Mountain tuff material. *Environmental Science & Technology*, 35: 2497-2504.
- Gao, B., Saiers, J.E. and Ryan, J.N., 2004. Deposition and mobilization of clay colloids in unsaturated porous media. *Water Resources Research*, 40(8): doi: 10.1029/2004WR003189.

- Gao, B., Saiers, J.E. and Ryan, J.N., 2006. Pore-scale mechanisms of colloid deposition and mobilization during steady and transient flow through unsaturated granular media. *Water Resources Research*, 42: W01410, doi: 10.1029/2005WR004233.
- Geckeis, H., Manh, T.N., Bouby, M. and Kim, J.I., 2003. Aquatic colloids relevant to radionuclide migration: Characterization by size fractionation and ICP-mass spectrometric detection. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 217: 101-108.
- Gerke, H. H. and van Genuchten, M. Th., 1993. Evaluation of a 1st-order water transfer term for variably saturated dual-porosity flow models. *Water Resources Research*, 29: 1225-1238.
- Gimbert, L.J., Haygarth, P.M., Beckett, R. and Worsfold, P.J., 2005. Comparison of centrifugation and filtration techniques for the size fractionation of colloidal material in soil suspensions using sedimentation field-flow fractionation. *Environmental Science & Technology*, 39: 1731-1735.
- Haitzer, M., Aiken, G.R. and Ryan, J.N., 2002. Binding of mercury(II) to dissolved organic matter: The role of the mercury-to-DOM concentration ratio. *Environmental Science & Technology*, 36: 3564-3570.
- Ho, C.H. and Miller, N.H., 1985. Effect of humic acid on uranium uptake by hematite particles. *Journal of Colloid and Interface Science*, 106: 281-288.
- Honeyman, B. D., 1999. Geochemistry -- Colloidal culprits in contamination. *Nature*, 397: 23-24.
- Huang, Y. and Saiers, J.E., in preparation. The influence of natural organic matter on mineral-colloid transport through variably saturated porous media. *Water Resources Research*.
- Jackson, B.P., Ranville, J.F., Bertsch, P.M. and Sowder, A.G., 2005. Characterization of colloidal and humic-bound Ni and U in the "dissolved" fraction of contaminated sediment extracts. *Environmental Science & Technology*, 39: 2478-2485.
- Jacobsen, O.H., Møldrup, P., de Jonge, H. and de Jonge, L.W., 1998. Mobilization and transport of natural colloids in a macroporous soil. *Physics and Chemistry of the Earth*, 23(2): 159-162.
- Jacobsen, O.H., Møldrup, P., Larsen, C., Konnerup, L. and Petersen, L.W., 1997. Particle transport in macropores of undisturbed soil columns. *Journal of Hydrology*, 196: 185-203.
- Jardine, P.M., Dunnivant, F.M., Selim, H.M. and McCarthy, J.F., 1992. Comparison of models for describing the transport of dissolved organic carbon in aquifer columns. *Soil Science Society of America Journal*, 56: 393-401.
- Jardine, P. M., Jacobs, G. K. and Wilson, G. V., 1993. Unsaturated transport processes in undisturbed heterogeneous porous media: I. Inorganic contaminants. *Soil Science Society of America Journal*, 57: 945-953.
- Jardine, P. M., Mayes, M. A., Mulholland, P. J., Hanson, P. J., Tarver, J. R., Luxmoore, R. J., McCarthy, J. F. and Wilson, G. V., 2006. Vadose zone flow and transport of dissolved organic carbon at multiple scales in humid regimes. *Vadose Zone Journal*, 5: 140-152.
- Jardine, P. M., Weber, N. L. and McCarthy, J. F., 1989. Mechanisms of dissolved organic carbon adsorption on soil. *Soil Science Society of America Journal*, 53: 1378-1385.
- Jardine, P. M., Wilson, G. V. and Luxmoore, R. J., 1988. Modeling the transport of inorganic ions through undisturbed soil columns from two contrasting watersheds. *Soil Science Society of America Journal*, 52: 1252-1259.
- Jardine, P. M., Wilson, G. V. and Luxmoore, R. J., 1990. Unsaturated solute transport through a forest soil during rain events. *Geoderma*, 46: 103-118.
- Jardine, P. M., Wilson, G. V., McCarthy, J. F., Luxmoore, R. J. and Taylor, D. L., 1990. Hydrogeochemical processes controlling the transport of dissolved organic carbon through a forested hillslope. *Journal of Contaminant Hydrology*, 6: 3-19.

- Jewett, D., Logan, B., Arnold, R. and Bales, R., 1999. Transport of *Pseudomonas fluorescens* strain P17 through quartz sand columns as a function of water content. *Journal of Contaminant Hydrology*, 36: 73-89.
- Jin, Y., Chu, Y. and Li, Y., 2000. Virus removal and transport in saturated and unsaturated sand columns. *Journal of Contaminant Hydrology*, 43: 111-128.
- Johnson, W. and Amy, G., 1995. Facilitated transport and enhanced desorption of polycyclic aromatic hydrocarbons by natural organic matter in aquifer sediments. *Environmental Science & Technology*, 29: 807-817.
- Johnson, W., Bao, G. and John, W.W., 2002. Specific UV absorbance of Aldrich humic acid: Changes during transport in aquifer sediment. *Environmental Science & Technology*, 36: 608-616.
- Kaplan, D.I., Bertsch, P.M., Adriano, D.C. and Miller, W.P., 1993. Soil-borne mobile colloids as influenced by water flow and organic carbon. *Environmental Science & Technology*, 27: 1193-1200.
- Keller, A.A. and Sirivithayapakorn, S., 2004. Transport of colloids in unsaturated media: Explaining large-scale behavior based on pore-scale mechanisms. *Water Resources Research*, 40: doi: 10.1029/2004WR003315.
- Kersting, A.B., Efur, D.W., Rokop, D.L.F.D.J., Smith, D.K. and Thompson, J.L., 1999. Migration of plutonium in ground water at the Nevada Test Site. *Nature*, 397: 56-59.
- Killey, R.W.D., McHugh, J.O., Champ, D.R., Cooper, E.L. and Young, J.L., 1984. Subsurface cobalt-60 migration from a low-level waste disposal site. *Environmental Science & Technology*, 18: 148-157.
- Lægdsmand, M., Villholth, K.G., Ullum, M. and Jensen, K.H., 1999. Processes of colloid mobilization and transport in macroporous soil monoliths. *Geoderma*, 93: 33-59.
- Lenhart, J.J. and Honeyman, B.D., 1999. Uranium(VI) sorption to hematite in the presence of humic acid. *Geochimica et Cosmochimica Acta*, 63: 2891-2901.
- Lenhart, J.J. and Saiers, J.E., 2002. Transport of silica colloids through unsaturated porous media: Experimental results and model comparisons. *Environmental Science & Technology*, 36: 769-777.
- Lenhart, J.J. and Saiers, J.E., 2004. Adsorption of natural organic matter to air-water interfaces during transport through unsaturated porous media. *Environmental Science & Technology*, 38: 120-126.
- Levi, B. G., 1999. Plutonium may be hitching a ride on colloids. *Physics Today*, 52: 19-20.
- Litaor, M. I., Barth, G. R. and Zika, E. M., 1996. Fate and transport of plutonium-239 + 240 and americium-241 in the soil of Rocky Flats, Colorado. *Journal of Environmental Quality*, 25: 671-683.
- Litaor, M. I., Barth, G. R., Zika, E. M., Litus, G., Moffitt, J. and Daniels, H., 1998. The behavior of radionuclides in the soils of Rocky Flats, Colorado. *Journal of Environmental Radioactivity*, 38: 17-46.
- Lu, N. and Mason, C.F.V., 2001. Sorption-desorption behavior of strontium-85 onto montmorillonite and silica colloids. *Applied Geochemistry*, 16: 1653-1662.
- Luxmoore, R. J., 1981. Micro-, meso-, and macroporosity of soil. *Soil Science Society of America Journal*, 45: 671-672.
- Luxmoore, R. J. and Abner, C. H., 1987. Field facilities for subsurface transport research. Report DOE/ER-0329, U.S. Department of Energy, Washington, DC.
- Luxmoore, R. J., Jardine, P. M., Wilson, G. V., Jones, J. R. and Zelazny, L. W., 1990. Physical and chemical controls of preferred path flow through a forested hillslope. *Geoderma*, 46: 139-154.

- Mahler, B.J., Bennet, P.C. and Zimmerman, M., 1998. Lanthanide-labeled clay: A new method for tracing sediment transport in a karst aquifer. *Ground Water*, 36: 835-843.
- Mayes, M. A., Jardine, P. M., Mehlhorn, T. L., Bjornstad, B. N., Ladd, J. L. and Zachara, J. M., 2003. Hydrologic processes controlling the transport of contaminants in humid region structured soils and semi-arid laminated sediments. *Journal of Hydrology*, 275: 141-161.
- McCarthy, J.F., 1998. Colloid-facilitated transport of contaminants in groundwater: Mobilization of transuranic radionuclides from disposal trenches by natural organic matter. *Physics and Chemistry of The Earth*, 23: 171-178.
- McCarthy, J.F., Sanford, W.E. and Stafford, P.L., 1998. Lanthanide field tracers demonstrate enhanced transport of transuranic radionuclides by natural organic matter. *Environmental Science & Technology*, 32: 3901-3906.
- McCarthy, J.F. and Zachara, J.M., 1989. Subsurface transport of contaminants. *Environmental Science & Technology*, 26(3): 586-593.
- Moridis, G. J., Hu, Q., Wu, Y.-S. and Bodvarsson, G. S., 2003. Preliminary 3-D site-scale studies of radioactive colloid transport in the unsaturated zone at Yucca Mountain, Nevada. *Journal of Contaminant Hydrology*, 60: 251-286.
- Murphy, R.J., Lenhart, J.J. and Honeyman, B.D., 1999. The sorption of thorium(IV) and uranium(VI) to hematite in the presence of natural organic matter. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 157: 47-62.
- Nelson, D.M., Penrose, W.R., Karttunen, J.O. and Mehlhaff, P., 1985. Effects of dissolved organic carbon on the adsorption properties of plutonium in natural waters. *Environmental Science & Technology*, 19: 127-131.
- Noell, A.L., Thompson, J.L., Corapcioglu, M.Y. and Triay, I.R., 1998. The role of silica colloids on facilitated cesium transport through glass bead columns and modeling. *Journal of Contaminant Hydrology*, 31: 23-56.
- Pace, M. N., Mayes, M. A., Jardine, P. M., Mehlhorn, T. L., Zachara, J. M. and Bjornstad, B. N., 2003. Quantifying the effects of small-scale heterogeneities on flow and transport in undisturbed cores from the Hanford Formation. *Vadose Zone Journal*, 2: 664-676.
- Payne, T.E., Davis, J.A. and Waite, T.D., 1996. Uranium adsorption on ferrihydrite -- effects of phosphate and humic acid. *Radiochimica Acta*, 74: 239-243.
- Pilgrim, D.H. and Huff, D.D., 1983. Suspended sediment in rapid subsurface stormflow on a large field plot. *Earth Surface Processes and Landforms*, 8: 451-463.
- Puls, R.W. and Powell, R.M., 1992. Transport of inorganic colloids through natural aquifer material: Implications for contaminant transport. *Environmental Science & Technology*, 26: 614-621.
- Righetto, L., Bidoglio, G., Azimonti, G. and Bellobono, I.R., 1991. Competitive actinide interaction in colloidal humic acid-mineral oxide systems. *Environmental Science & Technology*, 25: 1913-1919.
- Roberts, K.A., Santschi, P.H., Leppard, G.G. and West, M.M., 2004. Characterization of organic-rich colloids from surface and ground waters at the actinide-contaminated Rocky Flats Environmental Technology Site (RFETS), Colorado, USA. 2004. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 244: 105-111.
- Roy, S.B. and Dzombak, D.A., 1997. Chemical factors influencing colloid-facilitated transport of contaminants in porous media. *Environmental Science & Technology*, 31: 656-664.
- Roy, S.B. and Dzombak, D.A., 1998. Sorption nonequilibrium effects on colloid-enhanced transport of hydrophobic organic compounds in porous media. *Journal of Contaminant Hydrology*, 30: 179-200.

- Ryan, J.N. and Elimelech, M., 1996. Colloid mobilization and transport in groundwater. *Colloids and Surfaces A: Physicochemical Engineering Aspects*, 107: 1-52.
- Ryan, J.N., Elimelech, M., Baeseman, J.L. and Magelky, R.D., 2000. Silica-coated titania and zirconia colloids of subsurface transport field experiments. *Environmental Science & Technology*, 34: 2000-2005.
- Ryan, J.N., Illangasekare, T.H., Litaor, M.I. and Shannon, R., 1998. Particle and plutonium mobilization in macroporous soils during rainfall simulations. *Environmental Science & Technology*, 32: 476-482.
- Saada, A., Breeze, D., Crouzet, C., Cornu, S. and Baranger, P., 2003. Adsorption of arsenic(V) on kaolinite and on kaolinite-humic acid complexes: Role of humic acid nitrogen groups. *Chemosphere*, 51: 757-763.
- Saiers, J.E., 2002. Laboratory observations and mathematical modeling of colloid-facilitated contaminant transport in chemically heterogeneous systems. *Water Resources Research*, 38(4): doi: 10.1029/2001WR000320.
- Saiers, J.E. and Hornberger, G.M., 1996a. The role of colloidal kaolinite in the transport of cesium through laboratory sand columns. *Water Resources Research*, 32: 33-41.
- Saiers, J.E. and Hornberger, G.M., 1996b. Modeling bacterial-facilitated transport of DDT. *Water Resources Research*, 32: 1455-1459.
- Saiers, J.E. and Hornberger, G.M., 1999. The influence of ionic strength on the facilitated transport of cesium by kaolinite colloids. *Water Resources Research*, 35(6): 1713-1727.
- Saiers, J.E., Hornberger, G.M., Gower, D.B. and Herman, J.S., 2003. The role of moving air-water interfaces in colloid mobilization within the vadose zone. *Geophysical Research Letters*, 30(21): 2083, doi:10.1029/2003GL018418.
- Saiers, J.E. and Lenhart, J.J., 2003a. Ionic-strength effects on colloid transport and interfacial reactions in partially saturated porous media. *Water Resources Research*, 39(9): 1256, doi:10.1029/2002WR001887.
- Saiers, J.E. and Lenhart, J.J., 2003b. Colloid mobilization and transport within unsaturated porous media under transient-flow conditions. *Water Resources Research*, 39(1): 1019, doi:10.1029/2002WR001370.
- Saiers, J.E. and Ryan, J.N., 2005. Colloid deposition on non-ideal porous media: The influences of collector shape and roughness on the single-collector efficiency. *Geophysical Research Letters*, 32: L21406, doi: 10.1029/2005GL024343.
- Santschi, P. H., Roberts, K. A. and Guo, L., 2002. Organic nature of colloidal actinides transport in surface water environments. *Environmental Science & Technology*, 36: 3711-3719.
- Sätmark, B., Albinsson, Y. and Liang, L., 1996. Chemical effects of goethite colloids on the transport of radionuclides through a quartz-packed column. *Journal of Contaminant Hydrology*, 21: 231-241.
- Schäfer, A., Ustohal, P., Harms, H., Stauffer, F., Dracos, T. and Zehnder, A., 1998. Transport of bacteria in unsaturated porous media. *Journal of Contaminant Hydrology*, 33: 149-169.
- Schelde, K., Møldrup, P., Jacobsen, O.H., Jonge, H.D., Jonge, L.W.D. and Komatsuc, T., 2002. Diffusion-limited mobilization and transport of natural colloids in macroporous soil. *Vadose Zone Journal*, 1: 125-136.
- Schmitt, D., Saravia, F., Frimmel, F.H. and Schuessler, W., 2003. NOM-facilitated transport of metal ions in aquifers: Importance of complex-dissociation kinetics and colloid formation. *Water Research*, 37: 3541-3550.
- Sen, T.K., P., M.S. and Khilar, K.C., 2002. Adsorption of Cu^{2+} and Ni^{2+} on iron oxide and kaolin and its importance on Ni^{2+} transport in porous media. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 211: 91-102.

- Simeoni, M.A., Batts, B.D. and McRae, C., 2003. Effect of groundwater fulvic acid on the adsorption of arsenate by ferrihydrite and gibbsite. *Applied Geochemistry*, 18: 1507-1515.
- Sirivithayapakorn, S. and Keller, A., 2003. Transport of colloids in unsaturated porous media: a pore-scale observation of processes during the dissolution of the air-water interface. *Water Resources Research*, 39: 1346, doi: 10.1029/2003WR002487.
- Sprague, L.A., Herman, J.S., Hornberger, G.M. and Mills, A.L., 2000. Atrazine adsorption and colloid-facilitated transport through the unsaturated zone. *Journal of Environmental Quality*, 29: 1632-1641.
- Tipping, E., 2002. *Cation Binding by Humic Substances*. Cambridge University Press, Cambridge, UK.
- Torok, J., Buckley, L.P. and Woods, B.L., 1990. The separation of radionuclide migration by solution and particle transport in soil. *Journal of Contaminant Hydrology*, 6: 185-203.
- Triay, I., Simmons, A., Levy, S., Nelson, S., Nuttall, H., Robinson, B., Steinkampf, W. and Viani, B., 1995. Colloid-facilitated radionuclide transport at Yucca Mountain. Report LA-12779-MS, Los Alamos National Laboratory, Los Alamos, NM, 24 pp.
- Tuller, M. and Or, D., 2001. Hydraulic conductivity of variably saturated porous media: Film and corner flow in angular pores. *Water Resources Research*, 37: 1257-1276.
- Tuller, M., Or, D. and Dudley, L.M., 1999. Adsorption and capillary condensation in porous media: Liquid retention and interfacial configurations in angular pores. *Water Resources Research*, 35: 1949-1964.
- Turner, N., Ryan, J.N. and Saiers, J.E., 2006. The effect of desorption kinetics on colloid-facilitated transport of contaminants: Cesium, strontium, illite colloids, and a saturated quartz porous medium. *Water Resources Research*, 42: W12S09, doi:10.1029/2006WR004972.
- Turner, N., Ryan, J.N. and Saiers, J.E., in review. Kinetics of cesium and strontium desorption from clay mineral colloids in a saturated quartz porous medium. *Environmental Science & Technology*.
- Um, W. and Papelis, C., 2002. Geochemical effects on colloid-facilitated metal transport through zeolitized tuffs from the Nevada Test Site. *Environmental Geology*, 43: 209-218.
- Vilks, P.J., Cramer, J., Bachinski, D.B., Doern, D.C. and Miller, H.G., 1993. Studies of colloids and suspended particles, Cigar Lake uranium deposit, Saskatchewan, Canada. *Applied Geochemistry*, 8: 605-616.
- Vinten, A.J.A., Yaron, B. and Nye, P.H., 1983. Vertical transport of pesticides into soil when adsorbed on suspended particles. *Journal of Agricultural Food Chemistry*, 31(3): 662-664.
- Vogel, T., Gerke, H.H., Zhang, R. and van Genuchten, M.T., 2000. Modeling flow and transport in a two-dimensional dual-permeability system with spatially variable hydraulic conductivity. *Journal of Hydrology*, 238: 78-89.
- Wan, J. and Tokunaga, T.K., 1997. Film straining of colloids in unsaturated porous media: conceptual model and experimental testing. *Environmental Science & Technology*, 31: 2413-2420.
- Wan, J. and Wilson, J.L., 1994a. Colloid transport in unsaturated porous media. *Water Resources Research*, 30(4): 857-864.
- Wan, J. and Wilson, J.L., 1994b. Visualization of the role of the gas-water interface on the fate and transport of colloids in porous media. *Water Resources Research*, 30(1): 11-23.
- Warwick, P.W., Hall, A., Pashley, V., Bryan, N.D. and Griffin, D., 2000. Modelling the effect of humic substances on the transport of europium through porous media: A comparison of equilibrium and equilibrium/kinetic models. *Journal of Contaminant Hydrology*, 42: 19-34.
- Weigand, H. and Totsche, K.U., 1998. Flow and reactivity effects on dissolved organic matter transport in soil columns. *Soil Science Society of America Journal*, 62: 1268-1274.

- Weisbrod, N., Dahan, O. and Adar, E.M., 2002. Particle transport in unsaturated fractured chalk under arid conditions. *Journal of Contaminant Hydrology*, 56: 117-136.
- Wilson, G. V., Alfonsi, J. M. and Jardine, P. M., 1989. Spatial variability of subsoil hydraulic properties of two forested watersheds. *Soil Science Society of America Journal*, 53: 679-685.
- Wilson, G.V., and R.J. Luxmoore, 1988. Infiltration, macroporosity, and mesoporosity distributions on two forested watersheds. *Soil Science Society of America Journal*, 52: 329-335.
- Xu, S., Liao, Q. and Saiers, J.E., in review. Straining of non-spherical colloids within saturated porous media. *Environmental Science & Technology*.
- Xu, S. and Saiers, J.E., in preparation. Straining of heterodisperse colloidal suspension in water-saturated quartz sand. *Environmental Science & Technology*.
- Zhuang, J., Flury, M. and Jin, Y., 2003. Colloid-facilitated Cs transport through water-saturated Hanford sediment and Ottawa sand. *Environmental Science & Technology*, 37: 4905-4911.