Final Report

The Role of Natural Organic Matter and Mineral Colloids in the Transport of Contaminants through Heterogeneous Vadose-Zone Environments

James Saiers, Yale University (PI)
Joseph Ryan, University of Colorado (Co-PI)

Overview

James Saiers (Yale University) and Joseph Ryan (University of Colorado at Boulder) have been investigating colloid and colloid-associated contaminant transport in the vadose zone with funding from the U.S. Department of Energy's Environmental Remediation Sciences Division (ERSD). This research was initiated in the fall of 2002 with awards made to Yale University (Saiers PI, $120,000 per year, DE-FG07-02ER6349) and the University of Colorado (Ryan PI, $77,000 per year, DE-FG07-02ER63492; September 2002 to September 2005). The funding was extended in February 2006 with new two-year awards (Yale University, $144,000 per year, DE-FG02-06ER64188; University of Colorado, $131,000 per year, DE-FG02-06ER64189; February 2006 to February 2008). Findings from this research have been reported in ten manuscripts that have been published or submitted for publication (Box 1). Several more manuscripts are in preparation and will be submitted. We also have presented our research at numerous scientific conferences in the U.S. and Europe (Box 2).

Box 1. Peer-reviewed papers attributed to the Yale and University of Colorado ERSD grants: published and in review.

DeNovio, N.M. and J.N. Ryan, in review. Using particle size to evaluate particle mobilization mechanisms in unsaturated sand columns during simulated rainfall. *Environmental Science & Technology*.

Gao, B., J.E. Saiers, and J.N. Ryan, 2004. Deposition and mobilization of clay colloids in unsaturated porous media. *Water Resources Research*, **40(8)**, W08602, doi: 10.1029/2004WR003189.

Gao, B. J. E. Saiers, and J.N. Ryan, 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.

Saiers, J.E. and J.N. Ryan, 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.

Saiers, J.E. and J.N. Ryan. 2006, Introduction to Special Section on Colloid Transport in Subsurface Environments. *Water Resources Research*, **42**, W12S01, doi:10.1029/2006WR005620.

Turner, N. B., J.N. Ryan, and J.E. Saiers, 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., J.N. Ryan, and J.E. Saiers, in review. Kinetics of cesium and strontium desorption from clay mineral colloids in a saturated quartz porous medium. Submitted to *Environmental Science & Technology*, May, 2007.

Xu, S., B. Gao, and J.E. Saiers, 2006. Straining of colloidal particles in saturated porous media. *Water Resources Research*, **42**, W12S16, doi:10.1029/2006WR004948.

Xu, S., Liao, Q., Saiers, J.E, 2008. Straining of non-spherical colloids within saturated porous media. *Environmental Science & Technology*, 42, 771-778.

Xu, S. and J.E. Saiers. In review. Colloid straining within water-saturated porous media: Effects of colloid-size nonuniformity, *Water Resources Research*

Box 2. Presentations of research attributed to the Yale and University of Colorado ERSD grants.

Ryan, J.N., Turner, N. and Saiers. J., 2006. Colloids, contaminants, and surface chemistry: Effect of desorption kinetics on the facilitated transport of cesium and strontium by illite. *American Institute of Chemical Engineering 2006 Annual Meeting*, November 12-17, 2006, San Francisco, CA (<u>Invited</u>).

Ryan, J.N., J.E. Saiers, N.B. Turner, and T. Dittrich. 2006. A brief history of colloid-facilitated transport: Role of solute desorption kinetics. *Geological Society of America 2006 Annual Meeting*, October 22 – 25, 2006, Philadelphia, PA (<u>Invited</u>).

Ryan, J.N. and N.M. DeNovio, 2005. Effect of simulated rainfall on the transport of metals, organic matter, and colloids in a metal-contaminated flood plain soil. *International Workshop on Colloids and Colloid-Mediated Transport of Contaminants in Soils*, Bad Herrenalb, Germany, June 19-22, 2005 (<u>Invited</u>).

Saiers, J.E. 2006. Colloid transport through porous media. Gordon Research Conference, Proctor Academy, Andover, NH, July 30 – August 4, 2006 (<u>Invited</u>).

Saiers, J.E., B. Gao, and J.N. Ryan, 2005. Colloid deposition and mobilization mechanisms in unsaturated porous media during steady and transient flow. *General Assembly of the European Geosciences Union*, Vienna, Austria, April 25 - April 29, 2005 (<u>Invited</u>).

Saiers, J.E., Gao, B., Xu, S., and Ryan, J.N. 2005. Colloid mobilization and deposition in unsaturated Porous Media. *Geological Society of America 2005 Annual Meeting*, Salt Lake City, UT, October 16-19, 2005 (<u>Invited</u>).

Turner, N.B., J.N. Ryan, and J.E. Saiers, 2005. Effect of cation desorption kinetics on the colloid-facilitated transport of cesium and strontium. *Proceedings of the 229th ACS National Meeting*, San Diego, CA, March 13-17, 2005.

Study Goals

Our research was guided by a key objective of the Environmental Management Science Program (EMSP), which is to improve conceptual and predictive models for contaminant movement in complex vadose zone environments. Several studies, including some performed at sites inside the Department of Energy (DOE) complex, have documented the capacity of porewater mineral colloids to bind and to increase the transport rate of subsurface contaminants. It is now evident that OM also plays an important role in facilitating the transport of contaminants through soils.

The link between colloids and contaminant mobility is outlined in a recent Department of Energy report entitled *National Roadmap for Vadose Zone Science and Technology*. In this report, increases in the understanding of colloid-contaminant interactions, colloid mobilization, and colloid deposition within unsaturated soils are cited as requisite needs for predicting contaminant fate and distribution in the vadose zone. We addressed these needs by pursuing three key goals:

1. Identify the mechanisms that govern OM and mineral-colloid reaction and transport in heterogeneous, unsaturated porous media;
2. Quantify the role of OM and mineral colloids in scavenging and facilitating the transport of contaminants of concern to DOE; and

3. Develop and test a mathematical model suitable for simulating the movement of OM- and colloid-associated contaminants through heterogeneous, unsaturated porous media.

Relevance of Project to DOE Mission

About six billion cubic meters of soil at DOE sites are contaminated by radionuclides, metals, and dense non-aqueous phase liquids. Colloids and OM are capable of facilitating the subsurface transport of many of these contaminants. The first step in the transport of most of the contaminants from their sources to off-site surface water and groundwater is migration through the vadose zone. Developing our understanding of the migration of OM, colloids, and contaminants through the vadose zone is critical to assessing and controlling the release of contaminants from DOE sites. Facilitated transport is most important for contaminants that bind strongly to OM and mineral colloids. Some of the more prominent contaminants at DOE sites that are likely to associate with OM and mineral colloids include (1) the radionuclides plutonium, uranium, neptunium, americium, cesium, and possibly strontium; (2) the metals mercury and chromium (depending on their oxidation state) and (3) polychlorinated biphenyls present as dense non-aqueous phase liquids. Association of contaminants with OM and mineral colloids is only one criterion for colloid-facilitated transport. In addition, OM and colloids must be present in sufficient quantities to carry hazardous amounts of contaminants, and the transport of OM and colloids must be more rapid than that of the contaminants not associated with the OM and colloids. These criteria for facilitated transport are met at several DOE sites – the Nevada Test Site, the Oak Ridge National Laboratory, the Savannah River Site, the Hanford Reservation, and the former Rocky Flats site. Furthermore, colloid transport is being considered in the risk assessment for the Yucca Mountain high-level nuclear waste repository. The *National Roadmap for Vadose Zone Science and Technology* prescribes several tasks for understanding colloid-facilitated transport at DOE sites:

- Quantify colloid interactions with solid-water and air-water interfaces
- Quantify the effects of preferential flow on colloid transport
- Understand the effects of transient flow conditions on colloid-facilitated transport
- Characterize colloid-contaminant interactions as a function of solution chemistry and water saturation
- Characterize colloid transport in natural porous media (fine and coarse sands and fractured rock) as a function of solution chemistry and water saturation
- Model colloid transport and colloid-facilitated transport in unsaturated soils, sediments, and fractured rocks.

Our study directly addressed many of these tasks. We measured the mobilization of mineral colloids and OM in response to transients in porewater flow and perturbations in porewater chemistry. We explored the mechanisms that control colloid deposition and OM adsorption in heterogeneous porous media, while devoting special attention to the role of air-water interfaces in colloid and OM mass transfer. We quantified contaminant binding to mineral colloids and OM derived from DOE soils and evaluated the influences of these interactions on contaminant mobility. Finally, we continued to develop and refine a model for the transport of colloids, OM, and associated contaminants, building on previously published models of colloid-facilitated transport vadose-zone colloid transport, and OM transport.

Yale University and University of Colorado Research Findings on Colloid and Colloid-Facilitated Transport

We initiated our DOE-sponsored research with an investigation of colloid mobilization under unsaturated conditions. Our observations indicate that transients in porewater flow induce rapid colloid mobilization. Inorganic colloids composed of kaolinite and illite were mobilized in concentrations that exceeded 100 mg L^{-1} during column experiments conducted under transient-flow conditions typical of rainfall-induced infiltration events (*Gao et al.*, 2004). In these experiments, the mass of colloids mobilized during imbibition (wetting) of the porous medium was closely linked to the magnitude of the moisture-content increase, and the rate of colloid release scaled linearly with porewater velocity. We quantified this colloid-mobilization with a model that incorporated a simple parameterization scheme to distribute the colloid-release response over a range of moisture contents (*Gao et al.*, 2004).

Several mechanisms for colloid mobilization have been proposed. For example, some researchers report that hydrodynamic shear mobilizes colloids, while others contend that colloids are mobilized by electrostatic repulsion increased by the infiltration of rainfall of low ionic strength and carried to the mobile pore water by diffusion. To test the mobilization mechanism, we measured the rate of colloid mobilization during imbibition (wetting) of an unsaturated quartz sand medium using silica-coated colloids of two different sizes, 0.14 and 1.0 μm (*DeNovio and Ryan*, in review). Shear would mobilize the larger particles at a higher rate, while diffusion would transport the smaller particles at a higher rate. We observed that the smaller particles were mobilized at a higher rate (Figure 1) and that the kinetics of particle release was described well by a simple diffusion transport model.

Once mobilized, colloids move through the vadose zone by advection and dispersion and are susceptible to deposition by mass-transfer reactions that take place near air-water and solid-water interfaces. Results of our laboratory experiments showed that illite and kaolinite colloids exhibited high mobility over a range of moisture contents, although deposition reactions at air-water and solid-water interfaces did affect their transport (*Gao et al.*, 2004; *Huang and Saiers*, in preparation). Deposition of illite colloids was insensitive to changes in porewater pH and was probably dominated by straining within films of water that lined partially saturated pores. Kaolinite deposition, on the other hand, increased substantially as porewater pH declined and as the concentration of dissolved organic matter increased (Figure 2).
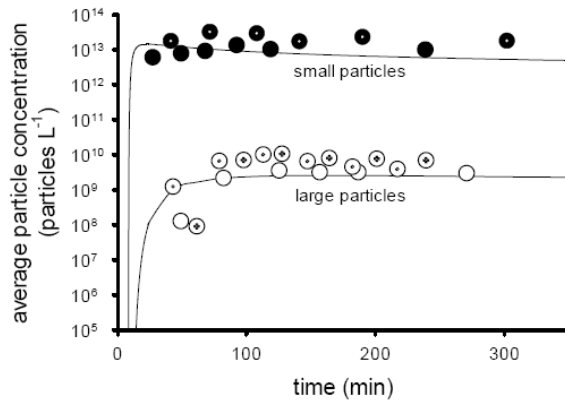

Figure 1. Particle concentration as function of time for small (0.14 μm) particles and large (1.0 μm) particles with the particle release rate modeled as a diffusive transport process (*DeNovio and Ryan*, in review).

We developed pore-scale visualization techniques to test our inferences on mechanisms that govern colloid deposition and mobilization in the column experiments (*Gao et al.*, 2006). In these experiments, a transparent flow cell packed with a thin layer of unsaturated sand was placed on a stage of an inverted microscope to permit direct observation of deposition and mobilization. Multiple mechanisms contributed to colloid deposition in the visualization experiments (*Gao et al.*, 2006). Insular air bubbles scavenged colloids, which is consistent with results of experiments conducted with etched micromodels. Colloids also were retained within thin films of water that stretched between pendular rings of unsaturated pores (Figure 3a) – results that confirm our previous speculation of the significance of film straining in influencing colloid mobility. Colloids were effectively immobilized upon entry and subsequent storage within zones of stagnant water (Figure 3b). This concept of stagnant-water zones has long been used to account for the storage of solutes, but, with very few
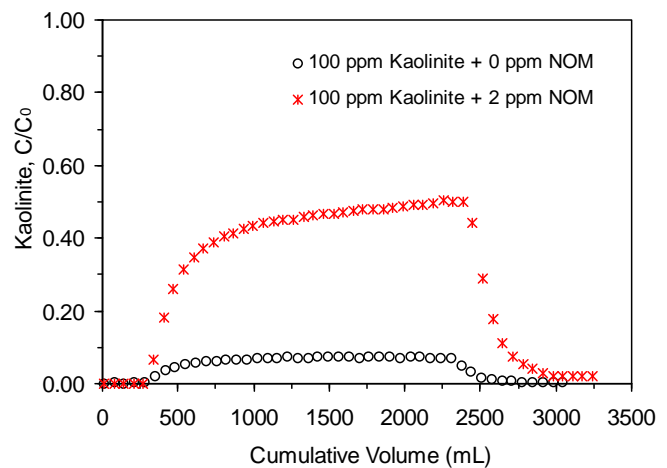

Figure 2. Kaolinite breakthrough curves measured in unsaturated sand column in the presence and absence of natural organic matter (NOM).

exceptions, has been ignored in descriptions of colloid transport and, prior to our work, no confirmatory evidence for stagnant-water storage of colloids existed.

The visualization experiments were especially useful in yielding insight into the mechanism that control colloid mobilization (*Gao et al.*, 2006). During transient porewater flow, characterized by temporal increases in moisture content, two mechanisms dominated the mobilization response. Film-strained colloids were released as the films were abruptly eliminated when partially saturated pores filled spontaneously with water. Porous-medium imbibition also promoted the release of colloids held within stagnant-water zones as water invaded air-filled regions of the porous medium and fragmented stagnant-water zones reconnected to areas of bulk fluid flow. The increases in flow rate that accompanied the moisture-content increases during the transient-flow experiments did not shear detectable quantities of colloids from the surfaces of the sand grains or insular air bubbles. Knowledge gained from these experiments is currently being used to refine the structure of our mathematical models that account for coupled transient porewater flow, colloid mobilization, and transport.

Even in our well-controlled laboratory systems, the porous medium is non-ideal, consisting of non-spherical mineral grains with considerable surface roughness. Published theoretical descriptions of colloid filtration, which were developed for water-saturated systems, are not designed to account for these non-idealities. One aspect of our research was devoted to modifying colloid-filtration theory to account for non-idealities associated with real geologic materials (*Saiers and Ryan*, 2005). Through statistical analysis of pore-scale simulations of laminar flow and convective-diffusive transport, we derived new correlation equations that express colloid-filtration rates in terms of porewater velocity, colloid size, and measurable indices that quantify mineral-grain shape and surface roughness. Our current results are only appropriate for water-saturated systems; however, we are
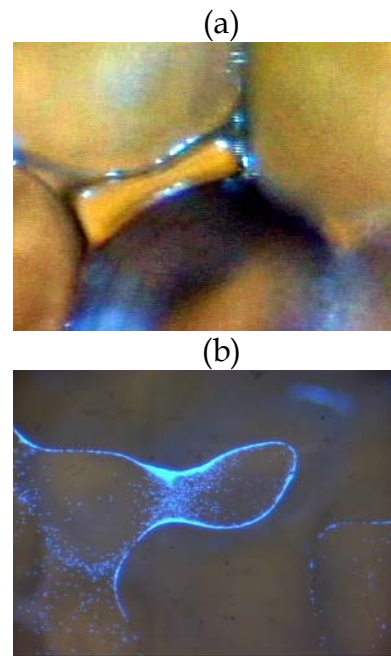
(a)

(b)

Figure 3. Pore-scale visualization of colloid immobilization: (a) colloids retained within thin films and pendular rings of a partially saturated pore (air occupies the center of the pore) and (b) colloids stored within stagnant-water regions that branch off from mobile-water regions (note colloid accumulation along perimeter of stagnant water zone at air-water boundary) (*Gao et al.*, 2006).

extending this analysis to account for complexities associated with water-unsaturated porous media.   We believe that this work will facilitate a shift from empirical descriptions of colloid deposition in the vadose zone to one in which colloid deposition can be predicted on the basis of measurable system properties.

We also examined the roles of colloid shape and colloid-size distribution in colloid filtration by straining (*Xu and Saiers*, in preparation; *Xu et al.*, in review). Findings from our research on colloid-shape effects demonstrate that straining rates of peanut-shaped colloids (Figure 4) are essentially identical to the straining rates of spherical colloids with diameters equal to the minor-axis length of the peanut-shaped colloids. This behavior is consistent with hydrodynamic-model simulations, which show that particles with spheroidal shapes preferentially align their long (major) axis with the direction of flow as they approach a pore constriction (*Xu et al.*, in review).
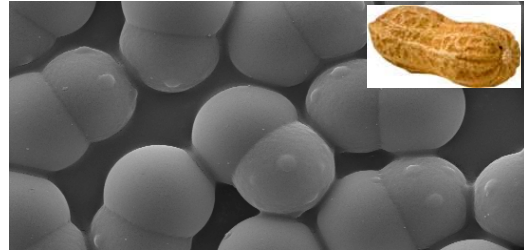

Figure 4. Peanut-shaped colloids (4.1 x 6.1 μm) used to study the influences of colloid shape on straining.

One of the key criteria for facilitated transport is that desorption of the contaminants from the colloids is slow relative to the transport time. Only if desorption is slow can colloids carry contaminants ahead of a contaminant plume. To test this criterion, we examined the facilitated transport of Cs^+ and Sr^{2+} by illite colloids in saturated flow-through columns and recirculating columns containing quartz sand (*Turner et al.*, 2006; *Turner et al.*, in review). The illite colloids transported cesium to a greater extent than strontium, and using an extension of the *Saiers and Hornberger* (1999) model of colloid-facilitated transport, we showed that desorption of strontium ions from the illite colloids was about fifty times as fast as that of the cesium. Slow desorption of cesium from illite was particularly evident at a very low Cs^+/illite ratio (10^{-8} mol g^{-1}) in the recirculating column. The cation desorption kinetics parameters are now being used to evaluate cesium and strontium transport in unsaturated columns of homogeneous and physically heterogeneous quartz sand.