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Effects of dissolved organic matter on the co-transport of mineral colloids and sorptive contaminants

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ABSTRACT

Colloid-facilitated transport of contaminants in the vadose zone has important implications to groundwater quality, and has received considerable attention. Natural organic matter (NOM) is ubiquitous in subsurface environments, and its influence on mineral colloids and solute transport has been well documented. However, research on the influence of NOM on colloid-facilitated transport is limited. The objective of this paper is to elucidate the effects of NOM on colloid-facilitated transport of a radioactive contaminant (Cs-137) within partially-saturated sediments. Measurements made with re-packed columns reveal that Cs-137 mobility was low when mineral colloids were absent and was unaffected by the presence of NOM. The addition of mineral colloids to influent increased Cs-137 mobility, and effluent Cs-137 was dominated by the colloid-associated form. When NOM was added to systems that contained mineral colloids and Cs-137, the mobility of Cs-137 further increased. A mathematical model simulating colloid-facilitated transport showed that NOM increases Cs-137 transport by increasing colloid mobility and reducing the rate of Cs-137 adsorption to the porous medium.

1. Introduction

Groundwater has been impacted by a variety of contaminants, many of which are discharged near land surface and enter groundwater through the vadose-zone track (Mattison et al., 2011). The transport of contaminants through the vadose zone has important implications to groundwater quality and has received considerable attention (e.g., Chen et al., 2005; Dresel et al., 2011; Lazouskaya et al., 2011, 2013; Masciopinto and Caputo, 2011; Oostrom et al., 2010; Unc et al., 2012). Dissolved contaminants are transported through vadose zone to groundwater by advection and dispersion, and the transport process can be retarded due to contaminant adsorption to the porous medium (Gidley et al., 2012; Rod et al., 2010; Roy and Dzombak, 1997; Simunek et al., 2006). For strongly adsorbing contaminants, the retardation is substantial and contaminant mobility could be limited if dissolved-phase transport is the only mechanism for contaminant migration. In the last few decades, it has been recognized that natural organic matter (NOM) and mineral colloids, both of which are ubiquitous in the vadose zone and groundwater, provide additional mechanisms for contaminant transport (e.g., Chen et al., 2005; Cheng and Saiers, 2010; Dunnivant et al., 1992; Kersting et al., 1999; Lowry et al., 2004; Sabbah et al., 2004; Yang et al., 2012). Mineral colloids and NOM have a high affinity for a variety of contaminants (e.g., heavy-metal ions, radionuclides, and organic molecules), and NOM and mineral colloids can, under some conditions, travel in a nearly conservative fashion or at least faster than sorptive aqueous-phase contaminants. Numerous laboratory studies and field observations have confirmed that colloid- or NOM-facilitated transport is an important mechanism for contaminant migration and can greatly increase contaminant mobility (e.g., Artinger et al., 2002a,b; Cheng and Saiers, 2010; Grant et al., 2011; Hartland

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et al., 2012; Kersting et al., 1999; Utsunomiya et al., 2009; Walshe et al., 2010; Yin et al., 2010).

Although extensive research has been conducted on the influence of NOM and mineral colloids on contaminant transport, fewer studies have been devoted to the synergistic effects of NOM and mineral colloids (Saiers, 2002; Tang and Weisbrod, 2009; Walshe et al., 2010; Wang et al., 2014, 2015). In natural subsurface environments, mineral colloids, NOM, and contaminants often co-exist. Studies have shown that NOM not only enhances mobility of mineral colloids (Akbour et al., 2002; Kretzschmar et al., 1995; Morales et al., 2011; Specht et al., 2000), but also changes equilibrium and kinetics of contaminant adsorption to minerals (Bouby et al., 2011; Kraemer et al., 2002; Lippold and Lippmann-Pipke, 2009; Saiers, 2002; Ticknor et al., 1996). Therefore, it is expected that colloid-facilitated contaminant transport will be affected by NOM. To quantify contaminant mobility under natural conditions, it is important to understand how contaminant-transport behavior is altered when both NOM and mineral colloids are present.

The objective of this paper is to advance understanding of the combined effects of mineral colloids and NOM on contaminant transport. We examined the transport of mineral colloids (i.e., illite and kaolinite) and Cs-137 in the absence and presence of NOM in laboratory column experiments. The columns were packed with clean quartz sand and Hanford coarse sand (HCS) to evaluate the influence of porous-medium mineralogy on colloid and Cs-137 mobility, and the experiments were conducted under both partially-saturated and water-saturated conditions. Data from the experiments were compared with calculations of a mathematical model for colloid-facilitated contaminant transport in order to quantify the effects of NOM on mineral-colloid deposition and Cs-137 adsorption/desorption to mobile and immobile solid phases.

2. Laboratory experiments

2.1. Preparation of materials

2.1.1. Porous media

Quartz sand (Accusand, Unimin Corp) was sieved to a size range of 0.355–0.425 mm and washed with de-ionized water, air dried, and stored in plastic containers. Uncontaminated (Cs-137 free) Hanford coarse sand (HCS) was collected from the 200E Submarine Pit of the Hanford site. The HCS is composed predominantly of quartz sand with lesser amounts of sodium/potassium feldspar, smectite, illite, chlorite, and kaolinite. The HCS has a median grain size of 1.7 mm, and mineral grains with dimensions between 1 mm and 5 mm compose 80% of its mass. The detailed information on HCS properties was described by Serne et al. (2002). The HCS was air-dried, sieved through a 2 mm sieve, homogenized by manual mixing with a plastic spade, and stored in plastic containers. The median grain size of the sieved HCS was approximately 1.2 mm, based on the HCS grain size distribution information (Serne et al., 2002).

2.1.2. NOM stock solution

Elliott soil humic acid (SHA) (1S102H, International Humic Substances Society) was used as a representative natural organic matter (NOM). NOM stock solution was prepared by dissolving 250 mg SHA into one liter electrolyte solution, which contained 9.84 mM NaCl and 0.16 mM $NaHCO_3$. NaOH was added to adjust the pH of the stock solution to 7.3. NOM stock solution was equilibrated overnight to ensure complete dissolution of the SHA.

2.1.3. Background solutions

Two types of background solutions were prepared. NOM-free background solution was prepared by dissolving NaCl and $NaHCO_3$ in de-ionized water. The concentrations of NaCl and $NaHCO_3$ equaled 9.84 and 0.16 mM, respectively, and the pH of this background electrolyte solution equaled 7.3. A second type of background solution had the same pH, NaCl and $NaHCO_3$ concentration as the NOM-free background solution, but was amended with NOM stock solution to a NOM concentration of 5 mg/L as dissolved organic carbon (DOC).

2.1.4. Mineral colloid stock suspension

Illite and kaolinite colloid stock suspensions were prepared by suspending 2 g illite powder (source clays repository) or kaolinite powder (VWR) in one liter NOM-free background electrolyte solution. The mixture was shaken vigorously, sonicated in water bath for 30 min, and transferred to a 1 L Erlenmeyer flask. After 24 h, the clay particles remaining in suspension were siphoned into a glass bottle and stored for subsequent use. Based on Stokes law, the colloids prepared as such have a hydrodynamic diameter of <2 μm (Saiers and Hornberger, 1999). Colloid concentration in kaolinite and illite stock suspensions were determined gravimetrically by filtering 50 mL of the suspension through a 0.1 μm membrane filter.

2.2. Batch adsorption experiments

The kinetics of Cs adsorption to quartz sand and HCS were studied using batch adsorption methods. Adsorption of Cs-137 to sand was measured as a function of time. Adsorption experiments were performed both in the presence and absence of NOM. Twenty four samples were prepared in 50-mL HDPE centrifuge tubes by adding 25 g of quartz sand (or 5 g of HCS) to an electrolyte solution ($I = 10$ mM) containing either 0 mg/L or 5 mg/L DOC. Following addition of 5.6×10^{-3} μmol/L Cs to each tube, the samples were capped and placed on a shaker table. At pre-determined time intervals (from a few minutes to 24 h), two replicate sample tubes were sacrificed for each experiment. The tubes were removed from the shaker, and supernatant was withdrawn from each tube, promptly filtered through 0.2 μm pore-size nylon filter, and analyzed for Cs concentration.

2.3. Column experiments

Cs transport through packed sand columns was studied in 12 experiments (Table 1). These experiments were distinguished on the basis of water saturation (partially saturated or saturated), porous media (quartz sand or HCS), concentration of DOC in pore water and influent suspension (0 or 5 mg/L), concentration of mineral colloids in the influent suspension (0 mg/L or 100 mg/L), and the type of mineral colloids (kaolinite or illite) of the column influent. For experiments