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Resupply mechanism to a contaminated aquifer: A laboratory study of U(VI) desorption from capillary fringe sediments

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Abstract

Contaminated capillary fringe sediments are believed to function as long-term source of U(VI) to Hanford's 300 Area groundwater uranium plume that discharges to the Columbia River. The deep vadose zone at this site experiences seasonal water table elevation and water compositional changes in response to Columbia River stage. Batch and column desorption experiments of U(VI) were performed on two mildly contaminated sediments from this system that vary in hydrologic position to ascertain their U(VI) release behavior and factors controlling it. Solid phase characterization of the sediments was performed to identify mineralogic and chemical factors controlling U(VI) desorption. Low adsorbed U(VI) concentrations prevented spectroscopic analysis. The desorption behavior of U(VI) was different for the two sediments in spite of similar chemical and textural characteristics, and non-carbonate mineralogy. Adsorption strength and sorbed U(VI) lability was higher in the near-river sediment. The inland sediment displayed low sorbed U(VI) lability (~10%) and measurable solid-phase carbonate content. Kinetic desorption was observed that was attributed to regeneration of labile U(VI) in the near river sediment, and carbonate mineral dissolution in the inland sediment. The desorption reaction was best described as an equilibrium surface complexation reaction. The noted differences in desorption behavior appear to result from U(VI) contamination and hydrologic history, as well as sediment carbonate content. Insights are provided on the dynamic adsorption/desorption behavior of contaminants in linked groundwater–river systems.

1. INTRODUCTION

Groundwater contaminants discharge to surface waters through a mixing zone where groundwater and river water interact (i.e., the hyporheic zone) (Ellis et al., 2007; Fritz et al., 2007). This mixing zone may extend over distances of meters to deca-meters depending on system scale. For hydraulically connected systems, seasonal oscillations in river stage cause groundwater flow reversals, and changes in water table elevation and groundwater composition that can strongly affect contaminant attenuation and transport (Chapman et al., 2007; Gandy et al., 2007). Contaminated aquifers that vary in water table exhibit complex behavior associated with water/solute storage within the seasonally saturated lower vadose zone, and its subsequent drainage and mixing with groundwater as water elevations fall (Lehmann et al., 1998; Henry and Smith, 2002). While these dynamic, coupled hydrologic systems are common worldwide, they are not well understood and few studies have investigated geochemical processes that control contaminant dynamics within them.

Uranium is a significant groundwater contaminant, and is regulated to low concentration (1.26×10^{-7} mol/L or 30 μg/L; http://www.epa.gov) in United States drinking waters because of health concern. Adsorption via surface complexation to mineral surfaces is an important geochemical process that concentrates U(VI) on aquifer solids, lowers its aqueous concentration, and slows its migration

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velocity in groundwater (Curtis et al., 2004, 2006). U(VI) surface complexation occurs on mineral forms common to subsurface sediments including: Fe(III) oxides (Waite et al., 1994; Duff and Amrhein, 1996; Gabriel et al., 1998; Bargar et al., 2000; Villalobos et al., 2001), phyllosilicates of different types (McKinley et al., 1995; Turner et al., 1996; Pabalan and Turner, 1997; Arnold et al., 1998, 2001; Chisholm-Brause et al., 2001, 2004), and quartz (Kohler et al., 1996; Pabalan et al., 1998). Aqueous carbonate concentration, pH, and $Ca^{2+}{}_{(aq)}$ regulate U(VI) surface complexation through their effects on U(VI) aqueous speciation, surface charge and electrostatic environment, and surface site mass balance (Waite et al., 1994; Villalobos et al., 2001; Davis et al., 2002; Dong and Brooks, 2006; Fox et al., 2006). The U(VI) surface complexation process is complex in subsurface sediments because of involvement of multiple sorbent types with variable and difficult to quantify site concentrations and local electrostatics (Davis et al., 1998). Consequently, simplified equilibrium surface complexation models have been used to describe U(VI) adsorption in subsurface sediments (Barnett et al., 2002; Davis et al., 2004; Um et al., 2007; Bond et al., 2008).

The forward (adsorption) and reverse (desorption) directions of U(VI) surface complexation in subsurface sediment may be slow and at disequilibrium as a result of diffusive mass transfer through reactive grain coatings and microporous lithic fragment interiors (Qafoku et al., 2005; Bond et al., 2008; Liu et al., 2008). Moreover, other poorly understood processes such as coprecipitation, intragrain precipitation, and absorption may create kinetic effects for U(VI) solid–liquid distribution at low concentration where surface complexation is the presumed reaction process (Giammar and Hering, 2001; Duff et al., 2002; Murakami et al., 2005).

Here we evaluate the desorption of behavior of U(VI) from two deep vadose zone sediments collected from a coupled, contaminated, aquifer–river system at the U.S. DOE Hanford site [300-FF-5; Williams et al. (2007)]. The groundwater U(VI) plume at this location has displayed remarkable persistence after source term removal for reasons that remain under debate. Groundwater U(VI) concentrations within the plume show dynamic seasonal behavior as a result of Columbia River stage changes, river water intrusion, water table oscillations, and associated geochemical interactions (Peterson et al., 2005, 2008). Two mildly contaminated sediments were collected from the deep vadose zone at elevations that can experience seasonal water saturation from water table changes. The sediments differ in their distance from the Columbia River, with one being near river and the other inland. Batch and column experiments were performed to simulate U(VI) desorption and release with water table change, and to ascertain whether U(VI) desorption from these sediments was of sufficient magnitude and longevity to sustain the contamination plume. Surface complexation modeling was used as an interpretive tool to assess solution composition and potential kinetic effects on desorption. Generalized insights result on the importance of equilibrium and kinetically controlled U(VI) desorption on reactive contaminant dynamics in coupled groundwater–river systems.

2. MATERIALS AND METHODS

2.1. Site description and sample collection

Nuclear fuels fabrication waste fluids were disposed to the 300 Area North Process Pond (NPP) and South Process Pond (SPP) and the 316-5 Process Trenches (316-5PT) between 1943 and 1973 to yield the largest in-ground inventory of U (47,550 kg) at the Hanford site (Zachara et al., 2005, 2007b). The two process ponds received most of the U inventory, and are within 200 m of the Columbia River. Waste components have infiltrated the 11 m vadose zone to produce a U(VI) plume in the underlying groundwater that discharges to the Columbia River (Young et al., 1990; Gerber, 1992). The plume extends well beyond the footprints of the two process ponds (Fig. 1) that were primary source terms. The highest historic U(VI) groundwater concentration [4.20×10^{-6} mol/L or ~1000 μg/L; Peterson et al. (2008)] has slowly decreased since the disposal activities ceased and contaminated near-surface sediments were excavated (McKinley et al., 2007; Williams et al., 2007). However, the groundwater U(VI) plume has not dissipated to drinking water standards (1.26×10^{-7} mol/L) through natural attenuation as expected by a CERCLA (Comprehensive Environmental Response, Compensation, and Liability Act) interim remedy issued in 1996 (Waichler and Yabusaki, 2005). Today, $U(VI)_{aq}$ concentrations within the plume are relatively low, ranging between 4.20×10^{-8} and 6.30×10^{-7} mol/L, or 10 and 150 μg/L (Fig. 1).

There have been numerous high river stage events during the lifetime of the plume that elevated the water table, and allowed contact of U(VI)-contaminated groundwater with deep vadose zone sediments that have adsorption affinity for U(VI). Such cyclic water table rise-and-fall events continue to this day, but are more controlled, seasonal, and dam-regulated. The water table changes by as much as 2 m between spring and fall. Contaminated vadose zone sediments that result from these water table excursions are believed to serve as U(VI) sources to groundwater during high water table events (Peterson et al., 2008).

Near water table sediments C4999-11D [12.7 m below ground surface (bgs), termed 11D] and C5000-39B (7.01 m bgs, termed 39B) were collected by sonic drilling during the placement of monitoring wells at locations C4999 and C5000 (Fig. 1). The hydrogeology of these samples and the system as a whole are well described by Williams et al. (2007). The samples are representative of a "bath tub-like ring" of elevated, adsorbed U(VI) that is found in the zone of seasonal water table fluctuation at multiple locations in the plume. These particular samples are different from those studied by Qafoku (2005), Liu (2008), and Bond (2008), in that they were collected from outside the footprint of the historic process ponds and were not subject to vertical contaminant fluxes [U(VI), Cu^{2+}, H^{+}, and OH^{-}] from above.

The two studied sediments have experienced different contaminant contact histories and hydrogeochemical conditions. Sample 11D was collected immediately down-gradient of SPP (the earliest site of waste disposal in 1941), and close to the Columbia River (Fig. 1). It has experienced frequent contact with U(VI) containing groundwaters; a maximum frequency of water table fluctuations; and large variations in bathing