Transport of U(VI) through sediments amended with phosphate to induce *in situ* uranium immobilization

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Abstract

Phosphate amendments can be added to U(VI)-contaminated subsurface environments to promote *in situ* remediation. The primary objective of this study was to evaluate the impacts of phosphate addition on the transport of U(VI) through contaminated sediments. In batch experiments using sediments (<2 mm size fraction) from a site in Rifle, Colorado, U(VI) only weakly adsorbed due to the dominance of the aqueous speciation by Ca-U(VI)-carbonate complexes. Column experiments with these sediments were performed with flow rates that correspond to a groundwater velocity of 1.1 m/day. In the absence of phosphate, the sediments took up 1.68 – 1.98 $\mu\text{g U/g}$ of sediments when the synthetic groundwater influent contained 4 $\mu\text{M U(VI)}$. When U(VI)-free influents were then introduced with and without phosphate, substantially more uranium was retained within the column when phosphate was present in the influent. Sequential extractions of sediments from the columns revealed that uranium was uniformly distributed along the length of the columns and was primarily in forms that could be extracted by ion exchange and contact with a weak acid. Laser induced fluorescence spectroscopy (LIFS) analysis along with sequential extraction results suggest adsorption as the dominant uranium uptake mechanism. The response of dissolved uranium concentrations to stopped-flow events and the comparison of experimental data with simulations from a simple reactive transport model indicated that uranium adsorption to and desorption from the sediments was not always at local equilibrium.

Keywords: Uranium, Phosphate, In Situ Immobilization, Reactive transport, Sequential extractions, CXTFIT

1. Introduction

Uranium contamination of soil and groundwater at more than 120 sites across 36 states in the United States has occurred as a result of activities associated with production of nuclear materials (Palmisano and Hazen 2003). The widespread contamination at many sites makes it economically challenging to use pump-and-treat or excavation methods for remediation. An alternative approach is to manipulate the chemical or physical conditions of the subsurface environment to promote *in situ* immobilization of uranium via formation of stable solid forms of uranium (Ahmed et al. 2012, Crane et al. 2011, Sharp et al. 2011a). Two widely studied classes of solids are U(IV) oxides (UO_{2+x}) with uraninite (UO_2) as the pure oxide form and autunite-group U(VI) phosphate solids that include autunite ($\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2$), sodium autunite ($\text{Na}_2(\text{UO}_2)_2(\text{PO}_4)_2$), and chernikovite ($\text{H}_3\text{O}(\text{UO}_2)(\text{PO}_4) \cdot 3\text{H}_2\text{O}$). Addition of phosphate amendments to U(VI)-contaminated subsurface environments has been evaluated in laboratory and field studies as a potential *in situ* remediation method (Arey et al. 1999, Beazley et al. 2011, Fuller et al. 2002, Mehta et al. 2014, Wellman et al. 2008). Phosphate addition can immobilize uranium by inducing the precipitation of low solubility U(VI) phosphate solids (Jensen et al. 1996, Singh et al. 2010). Various U(VI) phosphates have been observed at uranium-contaminated field sites (Arai et al. 2007, Buck et al. 1996, Catalano et al. 2006, Jones et al. 2001, Singer et al. 2009) and are also found in some ore settings without external addition of phosphate (Jerden et al. 2003).

In addition to helping to precipitate U(VI) solids, phosphate can influence U(VI) adsorption to mineral surfaces. Uranium sorption by ferrihydrite and goethite was enhanced in the presence of phosphate at weakly acidic pH because of the strong surface binding of phosphate and subsequent formation of ternary surface complexes (Cheng et al. 2004, Payne et

al. 1996, Singh et al. 2012). The presence of reactive mineral surfaces, like those of iron oxides and clays, can potentially limit the precipitation of U(VI) phosphate solids by adsorbing dissolved U(VI) and phosphate to make the solution less saturated with respect to potential precipitates or may facilitate heterogeneous nucleation of precipitates (Singh et al. 2010). Even U(VI) adsorption to calcium phosphate mineral surfaces can decrease the dissolved concentration of U(VI) to prevent U(V) phosphate precipitation (Fuller et al. 2002).

The primary objective of this study was to determine the impacts of phosphate addition on the transport of U(VI) through columns loaded with sediments from an environmentally relevant field site in Rifle, Colorado. Batch and column experiments were performed using these sediments with solutions that simulated the groundwater composition at the field site. Batch experiments were used to calculate the equilibrium uranium sorption capacity of Rifle sediments with synthetic groundwater in the absence and presence of added phosphate. Column experiments involved analysis of the influent and effluent solutions, reactive transport modeling, and characterization of the reacted sediments by sequential extractions and fluorescence spectroscopy. Insight into the processes controlling the impact of phosphate on U(VI) transport can help identify conditions that lead to the greatest reductions in U(VI) mobility.

2. Materials and Methods

2.1 Materials

All chemicals used in this study were ACS grade or better. Stock solutions were prepared in ultrapure water ($>18.2\text{ M}\Omega\text{-cm}$ resistivity). Background sediments ($<2\text{ mm}$ size fraction) from a uranium-contaminated site in Rifle, Colorado were used as the porous medium. Detailed characterization of these sediments has been reported previously (Campbell et al. 2012, Komlos et al. 2008). Campbell and co-workers reported that the background sediment samples have up

to 1.7 $\mu\text{g U/g}$ of sediments as determined from nitric acid extraction. XRD analysis of the sediments revealed the presence of quartz and plagioclase and potassium feldspars, with lesser amounts of amphibole, calcite, and clays. The clay size fraction is dominated by illite and smectite with minor amounts of chlorite and kaolinite. Mössbauer spectroscopy performed by Komlos et al. (2008) showed that iron is predominantly hosted in silicates and Al-rich goethite; the iron oxides hematite, magnetite, and ferrihydrite are also present but at lesser abundance.

2.2 Methods

2.2.1 Batch sorption experiments

The sediments were pre-equilibrated with synthetic Rifle groundwater (SRGW) (Table 1) under a 2.7 % CO_2 environment for 2 days under well-mixed conditions at a solids loading of 250 g/L. SRGW was prepared to simulate the conditions at the field site (Campbell et al. 2011, DOE 1999). This step was included to remove any labile background uranium. After pre-equilibration the sediments were separated from the solution and contacted with freshly prepared SRGW, spiked with varying concentrations of uranium (0.1 – 100 μM) and phosphate (0 – 1000 μM), and equilibrated for 2 days. Samples were then collected, filtered using 0.22 μm filters, and acidified to 1 % HNO_3 for elemental analysis. For the phosphate-free experiments and the lowest concentrations of U(VI), even after pre-equilibration some of the adsorption experiments resulted in final dissolved U concentrations greater than the initial concentrations. These samples were not included in the linear adsorption isotherm determination.

2.2.2 Column experiments

Column experiments were conducted at room temperature (22 ± 0.5 °C). Sediments were wet-loaded into glass columns (2.5 cm diameter x 15 cm length) and retained using porous plates (20

µm pore size) that also helped to distribute flow evenly to the column cross-section. This method resulted in porosity (θ) of 0.32 – 0.38 as determined from measurements of the sediment mass, total column volume, and volume of water needed to saturate the pore space. Plastic bags that were impermeable to gases (e.g., O₂ and CO₂) were used to store the SRGW, which allowed introduction of solutions with dissolved inorganic carbon concentration and solution pH that mimicked those at the actual site but that would have resulted in CO₂ exsolution to the ambient laboratory atmosphere. The SRGW was introduced into the columns in an upflow mode using a peristaltic pump at a rate (8 mL/h) that corresponded to a linear velocity of ~1.1 m/d, which was in the range observed at the site (Fang et al. 2009, Moon et al. 2010, Yabusaki et al. 2007).

Experiments were performed in different modes (Figure 1) that involved feeding SRGW to the columns with or without uranium and phosphate. A conditioning mode during which SRGW that did not contain uranium and phosphate was included to remove the background labile fraction of uranium from the sediments. Columns were then operated in an uptake mode until with 4 µM U(VI) in the influent until uranium breakthrough occurred. Finally a release mode was performed with uranium-free influents both with and without added phosphate. Bromide was included as a conservative tracer for calculating hydrodynamic transport parameters. A stopped flow technique described by (Brusseau et al. 1997) was used to observe the effects of non-equilibrium processes on uranium uptake and release. In this method, the flow was stopped to the columns for 12-hour periods and then restarted. Examination of the extent of uranium uptake by or release from the sediments during this stagnant period provides information regarding the mass transfer of chemical kinetic limitations to solid-water exchange of uranium. Column experiments were terminated at different times, and sediment samples were collected in increments from various depths (roughly 5 cm each) to study the speciation and

spatial distribution of uranium along the length of the column. The current study represents a scenario of a site with a relatively stable plume of uranium-contaminated groundwater into which phosphate solution is introduced.

Thermodynamic calculations using the latest critically reviewed database for uranium and relevant reactions (Mehta et al. 2014) determined that the SRGW solution was undersaturated with respect to any uranium solid phase. In the absence of phosphate, the solution was slightly supersaturated ($SI = 0.33$) with respect to calcite. In the presence of phosphate, the solution was supersaturated with calcium phosphates that included hydroxylapatite and octacalcium phosphate; however, no precipitates were visibly present in the influent reservoirs and influent samples indicated no loss of calcium or phosphate from the influent solution.

2.2.3 Chemical analysis of influent and effluent

Samples (influent and effluent) were regularly collected, analyzed for pH and bromide concentration, saved for dissolved inorganic carbon (DIC) analysis, and preserved for elemental analysis by acidifying to 1% HNO_3 . Dissolved concentrations of U, P, Ca, Na, Mg, K and Si were measured using inductively coupled plasma-mass spectrometry (ICP-MS, Perkin Elmer Elan DRC II). The ICP-MS detection limit was 0.1 $\mu g/L$ for uranium, 10 $\mu g/L$ for phosphorus, and 50 $\mu g/L$ for other measured elements. DIC was measured using a TOC analyzer (Shimadzu, TOC-L_{CPH/CPN} PC-controlled model). Bromide was measured with an ion selective electrode (Cole-Parmer).

2.2.4 Calculation of transport parameters

Bromide and uranium breakthrough and washout curves were used to calculate various transport parameters using the CXTFIT-Excel tool (Tang et al. 2009) originally based on the FORTRAN

version (Parker and Van Genuchten 1984) and modified by (Toride et al. 1995) to include the convection dispersion equation (CDE) solving capabilities. Equation 1 represents the generic form of the CDE assuming one-dimensional steady flow in a homogenous, isotropic porous medium.

$$R \frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} + r \quad (1)$$

where C = concentration in liquid phase [mol/m^3], t = time [s], D_L = longitudinal hydrodynamic dispersion coefficient [m^2/s], x = distance [m], v = average linear velocity [m/s], and r indicates the rate of a biological or chemical reaction (production/sink) [$\text{mol}/\text{m}^3\text{-s}$] of the solute other than sorption. R is the retardation factor, which is related to the partition coefficient (K_d) [m^3/kg] as shown in equation 2.

$$R = 1 + \frac{\rho_b K_d}{\theta} \quad (2)$$

where, ρ_b is the bulk density (kg/m^3) and θ is the porosity. As determined from the known column volume and the measured masses of the sediments and the water-saturated column, values of ρ_b ranged from 1740 to 1810 kg/m^3 and values of θ varied from 0.32 – 0.38 for different columns.

Equations 3 and 4 represent the dimensionless non-equilibrium CDE. The model is based on the assumption that the aqueous phase can be partitioned into mobile and immobile regions.

$$\beta R \frac{\partial C_m}{\partial T} = \frac{1}{Pe} \frac{\partial^2 C_m}{\partial X^2} - \frac{\partial C_m}{\partial X} - \omega(C_m - C_{im}) \quad (3)$$

$$(1 - \beta)R \frac{\partial C_{im}}{\partial T} = \omega(C_m - C_{im}) \quad (4)$$

where $T = vt/L$ and $X = x/L$ are dimensionless representations of time and distance along the column, and subscripts m and im indicate the mobile and immobilize zones respectively. Fitting of the model to experimental data was used to calculate the dimensionless parameters ω and β in equations 3 and 4. These parameters from the non-equilibrium CDE are then further based on properties of the columns and the processes indicated in equations 5 and 6.

$$\omega = \frac{\alpha L}{\theta v} \quad (5)$$

$$\beta = \frac{\theta_m + f \rho_b K_d}{\theta + \rho_b K_d} \quad (6)$$

where α is the first-order mass transfer coefficient (s^{-1}) governing the rate of solute exchange between the mobile and immobile liquid regions and f is the fraction of adsorption sites that equilibrates with the mobile liquid phase.

As would be expected for a non-reactive solute, bromide transport was not retarded through the column and its R value was set to 1. Effluent bromide and uranium data were simultaneously fit to determine the Peclet number (Pe), mobile water fraction (β), mass transfer coefficient (ω) and uranium retardation factor (R). The dispersivity (λ in cm) was determined using the Peclet number and length (L) of the column (Equation 7).

$$P_e = \frac{L}{\lambda} = \frac{L v}{D_L} \quad (7)$$

The retardation coefficient obtained through fitting was used to calculate the value of the partition coefficient K_d .

2.2.5 Sequential extractions

Sediments were collected in roughly three equal sections along the length of the column at the end of each experiment and classified as those from the inlet, midsection, and outlet. Extractions were performed in duplicate for all the column samples. A four step sequential extraction method (Table 2) modified from (Tessier et al. 1979) with a solid to solution ratio of 40 g/L (34 g dry weight/L based on moisture content measurements) in 50-mL reactors was used to evaluate the solid phase speciation and spatial distribution of uranium. A single step total digestion using a mixture of nitric acid and hydrochloric acid at 100° C for 4 h was also performed to more directly measure the total uranium content for comparison with the total content determined from the sum of the uranium amounts from the four steps of the sequential extraction. This hot acid extraction was determined to fully extract the uranium in the sediments based on comparisons with published total uranium contents for the site (Campbell et al., 2012) and in quality control tests using standard reference materials that indicated complete uranium recovery.

2.2.6 Laser induced fluorescence spectroscopy (LIFS) analysis

Sediment samples from different depths within a column were loaded into 2 mm × 4 mm x 25 mm quartz cuvettes for analysis. Instrumentation and experimental procedures for LIFS analysis have been described previously (Wang et al. 2004, Wang et al. 2005). The quartz cuvettes were attached to the cold finger of a CRYO Industries RC152 cryostat with liquid helium vaporizing beneath the sample to reach a sample temperature of 8 ± 2 K. The samples were excited with a Spectra-Physics Nd:YAG laser-pumped Lasertechnik-GWU MOPO laser at 415 nm, and the emitted light was collected at 85° to the excitation beam and detected with a thermoelectrically cooled Princeton Instruments PIMAX intensified CCD camera after spectral dispersion through an Acton SpectroPro 300i double monochromator spectrograph. The spectra were analyzed using the commercial software IGOR (Wavematrix, Inc).

3. Results and discussion

3.1 Batch sorption experiments

Increasing phosphate concentrations (0 – 1000 μM) resulted in increased uranium uptake for starting uranium concentrations of 0.1 – 100 μM (Figure 2). For a linear adsorption isotherm, K_d values of 0.4, 0.6 and 2.2 mL/g are calculated for 0, 100 and 1000 μM phosphate concentrations, respectively. Increased uranium uptake caused by phosphate could be due to the formation of inner-sphere U(VI)-phosphate ternary surface complexes that have previously been observed in the presence of phosphate and various iron-oxides (Bostick et al. 2002, Cheng et al. 2004, Payne et al. 1996, Singh et al. 2010). Uranium adsorption onto Rifle sediments could occur through cation exchange to interlayer sites in clays and inner-sphere binding to iron oxide surfaces or to edge sites on clays like montmorillonite. Surface complexes could include binary surface complexes as well as ternary surface complexes with phosphate as noted above as well as ternary surface complexes with carbonate (Bargar et al. 1999, Bernhard et al. 2001, Sherman et al. 2008). Both iron oxides and clays are present in this sediment (Campbell et al. 2012, Komlos et al. 2008).

Previous batch studies on uranium sorption in the absence of phosphate using background sediments from the Rifle site have measured K_d values up to 1.25 mL/g at pH 7.2 and 2.6 % CO_2 conditions (Hyun et al. 2009); the present study had pH 7.1 and ~ 2.7 % CO_2 . Adsorption of U(VI) by the Naturita aquifer sediments (another former uranium milling site in Colorado) had K_d values of ~ 3 mL/g at 1.6 % CO_2 (Davis et al. 2004). The lower K_d values under phosphate-free conditions observed in the present study may be due to slight differences in the chemical compositions of the solutions and to differences in the properties of the sediments collected at different sites or from different locations of the Rifle site. Several studies have found

K_d values to be very sensitive to CO_2 conditions (Hyun et al. 2009, Kohler et al. 1996, Reardon 1981). The higher calcium concentration (5 mM) in this study as compared to the 3 mM in Hyun et al. (2009) could also have inhibited sorption. For SRGW, in the presence or absence of phosphate, the U(VI) predominantly exist as $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ (~ 87 %) followed by $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ (~ 13 %). Higher calcium concentrations decrease U(VI) adsorption due to formation of stable aqueous Ca-UO₂-CO₃ ternary complexes (Bernhard et al. 1998, Bernhard et al. 2001, Dong and Brooks 2006, Stewart et al. 2010). Overall, the extent of adsorption to sediments with appreciable carbonate concentrations is lower than to other materials; batch adsorption experiments with sediments from the Oak Ridge, Savannah River, and Hanford Sites all had greater adsorption affinities for uranium than did the Rifle sediments. For these sediments, uranium desorption consistently decreased when the carbonate concentration was increased (Barnett et al. 2000). Hence, the extent of immobilization at the Rifle site is likely limited due to the high carbonate concentration.

The K_d values determined in the present study and previous work for the Rifle site are overall much lower than those determined for sediments from other sites. K_d values of 14 – 22 mL/g, 51 – 95 mL/g and 40 – 30000 mL/g have been determined for sediments from the Hanford site in Washington (Qafoku et al. 2005), Oak Ridge site in Tennessee (Stewart et al. 2010) and F-area Savannah River site in South Carolina (Dong et al. 2011), respectively. Differences in sediment mineralogy and groundwater composition may explain the different adsorption affinities found at various sites.

3.2 Uranium uptake and release in the absence of phosphate

3.2.1 Aqueous phase analysis

The conditioning mode flushed an appreciable amount (0.2 µg/g) of labile uranium from the initial sediments (Figure 3). During the uptake mode similar bromide breakthrough profiles were observed for all columns. As a conservative tracer, bromide concentrations increased rapidly to reach the influent level within 4 pore volumes (PV) as compared to ~ 35 PV required for uranium to achieve complete breakthrough (Figure 3). The greater pore volumes for U(VI) breakthrough directly indicate that its transport was retarded by adsorption to the sediments. Calculations based on a simple mass balance approach (equation 8) that accounts for the difference in influent and effluent concentrations determined uranium uptake of up to 1.98±0.14 µg/g of sediments (Table 3).

$$U_{mass\ uptake} \left(\frac{\mu g}{g} \right) = \frac{\sum [(C_{in} - C_{out}) * Q * t]}{m_{sed}} \quad (8)$$

where C_{in} and C_{out} are the measured uranium concentrations (µg/L), Q is the flow rate (L/h), t is the total time of flow at a given concentration (h), and m_{sed} is the mass of sediments in the column (g). The uncertainty estimates reported in Table 3 come from the propagation of uncertainty across the 10 or more effluent samples used in the summation in equation 8.

Uranium release was initiated following the uptake mode by introducing uranium-free SRGW both without (Column B) and with (Columns C and D) phosphate. In the absence of phosphate, all of the uranium that had been taken up during loading was desorbed from the sediments within 100 PV.

The stopped flow events revealed noticeable non-equilibrium sorption behavior for all columns. For these events during the uptake mode, the uranium concentrations were lower when flow was resumed than immediately before it was stopped, which indicates that during stopped flow the uranium was taken up by processes that could not reach local equilibrium with flowing

water. Uranium release was also influenced by the stopped flow event wherein the uranium concentrations increased when there was no flow. A similar phenomenon was observed for Hanford sediments in column experiments (Qafoku et al. 2005) in which the magnitude of change in concentrations was proportional to the duration of stopped flow. For 24-h stopped flow events with Hanford sediments, the U(VI) concentrations decreased by < 10 % during the adsorption phase. In the current study with only 12 h stopped flow events, the U(VI) concentrations decreased by ~ 10 % during the adsorption phase.

Non-equilibrium uranium adsorption could occur due to chemical (different adsorption kinetics) and/or physical (intraparticle diffusion) processes. Since the adsorption of U(VI) to mineral surfaces is generally fast, typically attaining equilibrium within few minutes (Giammar and Hering 2001, Hsi and Langmuir 1985), the non-equilibrium U(VI) adsorption behavior is believed to result from physical mass transfer processes. For example physical non-equilibrium models have been used previously to successfully simulate uranium transport in column and field-scale studies (Fox et al. 2012, Greskowiak et al. 2011, Qafoku et al. 2009). The non-equilibrium behavior of uranium in this study has thus been attributed to the intragrain diffusional mass transfer limitations existing within local micro-environments.

3.2.2 Simulating the reactive transport of uranium

Adsorption and release profiles for both uranium and bromide were fitted simultaneously for column B (Figure 4a), and only the adsorption profiles for uranium were fitted for columns A, C and D (Figure 4b). The desorption profiles for column C and D were not fitted because CXTFIT can only be used to fit adsorption-desorption modes with the same composition. It was likely that in the presence of phosphate, reactions other than adsorption-desorption of uranium were also occurring, and CXTFIT can only account for processes like adsorption that can be interpreted

using a simple partition constant. To be consistent with the stopped flow event observations, which indicated that local equilibrium was not achieved for the mobile fluid residence times of the experiments, a non-equilibrium CDE model using a single set of parameters was used to simulate uranium transport. Values of 4.62 for Pe, 0.55 for β , and 0.98 for ω provided the optimal fits to the data (Figure 4). These values yielded an f value of 0.50, λ of 3.25 cm and α ranging from 2.6×10^{-5} to $3.1 \times 10^{-5} \text{ s}^{-1}$. The Peclet number is consistent with longitudinal transport being primarily controlled by advection. The value of f indicates that the pore water is evenly distributed (i.e. 50% / 50%) between mobile and immobile phases. The α values are sufficiently large that even with 50% of the surface sites contained in immobile water the transfer of solutes from the mobile to immobile regions still allows considerable adsorption to intragranular sites to occur during flow. Values ranging from 0.19 – 2.99 and 0.37 – 0.60 have been reported for ω and β , respectively, from similar fitting of column experiments with clayey soils and investigation of tritiated water ($^3\text{H}_2\text{O}$) and boron (B) transport (Tang et al. 2009). The fitting exercise involved estimation of multiple parameters (Pe, β , R and ω) simultaneously to yield the optimal fit of the model to the data; however, other combinations of parameters may also be able to provide reasonable fits so the exact parameters determined are used primarily to illustrate that non-equilibrium processes are important for U(VI) transport in these sediments.

A retardation factor (R) of 10.85 was obtained through the fitting of uranium profiles which resulted in K_d values in the range of 1.90 – 2.03 mL/g using equation (2) based on linear isotherm assumptions. The range of K_d values obtained is similar to those previously determined for background sediments from Rifle area [up to 1.25 mL/g] (Hyun et al. 2009) and sediments from another former Uranium milling site in Colorado [~ 3 mL/g] (Davis et al. 2004); however, they are somewhat higher than the K_d of 0.4 mL/g determined from the present study's batch

experiments. R values of 87 – 127 were obtained by fitting uranium profiles in Hanford column experiments (Qafoku et al. 2005).

3.2.3 Sequential extractions

Sequential extractions provided important information about the amounts and speciation of uranium in the sediments. Uptake amounts calculated for column A using the influent-effluent mass balance approach ($1.9 \pm 0.1 \mu\text{g/g}$) were very similar to those obtained through sequential extractions ($2.1 \pm 0.7 \mu\text{g/g}$). The uncertainty estimate on the amounts from the sequential extractions comes from four separate sources: the difference in sequential extractions of duplicate samples, the summation of uranium in each extraction step, the averaging of the uranium content from extractions performed on the inlet, middle, and outlet zones of the columns, and from the difference between the total extracted uranium from Column A (column with adsorbed uranium) and Column B (column with all uranium desorbed and only including the initial background uranium). The uptake amounts calculated for columns B and D using two different methods were within 30 % of each other. Negligible amounts were extracted in the water soluble step. The dominant fractions of labile uranium were extracted in the step targeting ion exchangeable species and then in the weak acid extraction step (Figure 5a). Up to $1.5 \mu\text{g/g}$ of U was retrieved in the hot acid digestion step from the sediments both before and after loading of U in the columns. This amount of uranium is consistent with recalcitrant solid forms of uranium in the original Rifle sediments (Campbell et al. 2012) and was not included in the estimates of the amount of uranium taken up during the loading portion of the experiment. The amount of uranium in the background sediments shown in Figure 5 is for sediments that had undergone conditioning with SRGW that removed some labile U.

3.3 Uranium release in the presence of phosphate

3.3.1 Aqueous phase analysis

Uranium concentrations decreased faster for the phosphate-treated columns (Columns C and D) than for the column (Column B) that was not treated with phosphate (Figure 6). Although this observation might initially suggest that phosphate's presence resulted in faster uranium desorption, the influent-effluent mass balance for the column indicated that more than 75 % of the adsorbed uranium (1.51 $\mu\text{g/g}$) was retained over 100 PV of operation when phosphate was present (Column D) in the influent (Table 3). The more rapid decrease to low concentrations when phosphate was present was caused by enhanced retention of uranium by the sediments.

3.3.2 Sequential extractions

Sequential extraction results confirmed the observations regarding phosphate's effect on uranium retention. For sediments for which uranium was released after 132 PV of uranium and phosphate-free SRGW was flushed through the column (i.e. Column B, following the completion of the release mode), almost no uranium was detectable in the first three extraction steps (Figure 5b). In contrast, when phosphate was added to the uranium-free influent during the release mode, uranium retained was detectable and primarily in forms that could be mobilized by ammonium acetate and acetic acid (Figure 5c). The extractions were carried out at pH 7 (ammonium acetate) and pH 5 (acetic acid) and it is likely that not all adsorbed uranium was desorbed or that not all precipitated uranium solids dissolved. Enhanced retention caused by phosphate was probably due to adsorption or precipitation. Uniform distribution of uranium along the length of the column suggests that adsorption was the dominant uranium uptake mechanism. If uranium uptake had occurred through precipitation, then more uranium would have been expected near the inlet where maximum supersaturation would have occurred as the phosphate-containing influent first contacted the uranium-loaded sediments.

3.4 LIFS determination of likely U(VI) species present

Fluorescence spectra of samples from Column A showed very little or no discernible fluorescence spectral intensity (Figure 7). This behavior could be attributed to multiple reasons. First, a weak broad spectral background could result from surface complexes (Wang et al. 2005). Second, iron oxides in the sediments (Campbell et al. 2012, Komlos et al. 2008) could quench fluorescence at room temperatures and result in poorly resolved spectra (Wang et al. 2011). Finally, multiple quenching mechanisms are exhibited by the uranyl ion that could lead to spectral broadening at room temperatures (Wang et al. 2005). However, analyzing the samples at lower temperatures did not improve spectral intensities or resolution thereby suggesting that fluorescence quenching was likely the result of the presence of surface complexes.

Fluorescence spectra for samples from Columns B and D had similar features (weak, broad spectral background) to those for the samples from Column A. However, an additional weak feature was observed for the sample obtained from the inlet end of column D, one of the columns amended with phosphate (Figure 7). This additional feature does not match any of the peaks observed for uranyl phosphate solids and thus suggests the presence of a different uranyl species in addition to the surface complexes seen in samples from Column A. Addition of phosphate might have resulted in formation of ternary uranyl phosphate complexes that led to improved retention within the columns during the release phase or the precipitation of calcium-phosphate solid onto which uranium was then bound. These results imply that uranium immobilization occurred via adsorption. If the dominant mechanism had been precipitation, then uranium distribution within the column should have been uneven or sediments should have had distinct fluorescence spectral characteristics.

4. Conclusions

Aqueous phase and solid phase measurements demonstrate the enhanced retention of uranium caused by phosphate addition to sediments. Sequential extractions revealed that uranium was distributed uniformly within the columns. Higher retention in the presence of phosphate could be due to enhanced adsorption of uranium through the formation of ternary surface complexes. Batch sorption experiments confirmed that the K_d for uranium adsorption increases by up to a factor of 6 upon phosphate addition. Stopped flow events performed during the column experiments confirmed that non-equilibrium processes were involved in controlling the U(VI) transport during the adsorption and desorption modes. The non-equilibrium behavior is believed to result from physical mass transfer processes and is attributed to intragrain diffusional mass transfer limitations existing within local micro-environments.

A one-dimensional non-equilibrium CDE model was used to fit uranium and bromide profiles and calculate the transport parameters. Fitting of the uranium and bromide profiles yielded a retardation factor of 10.85 for uranium. Based on this retardation factor value, a distribution coefficient (K_d) was calculated that suggests that the Rifle sediments are relatively weak adsorbents for uranium compared to those at other sites. At low carbonate concentrations and at pH conditions ranging from slightly acidic to mildly alkaline, phosphate amendments may be more effective for *in situ* uranium immobilization than that would be at the Rifle site.

The current study represents a scenario of phosphate addition to a site with most of the uranium hosted within the sediments. The results from the examined scenario indicate that uranium retention in the sediments can be achieved by phosphate addition. However, the extent of this retention is relatively modest compared to the decreases in effluent uranium concentrations that can be achieved by sustained biological reduction (Sharp et al. 2011b) or that could potentially be achieved at sites with more favorable conditions for U(VI) adsorption..

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Figure Captions

Figure 1. Experimental modes of operation to study the transport of U(VI) through sediments amended with phosphate to induce *in situ* uranium immobilization.

Figure 2. Equilibrium uranium sorption on Rifle sediments (250 g/L) after 2 days of reaction with SRGW for three phosphate concentrations. Trendline(s) included for different starting phosphate concentrations were used to determine K_d values of 0.4, 0.6 and 2.2 mL/g for 0, 100, and 1000 μM P respectively. Only data points for which uranium uptake can be unambiguously assigned to adsorption have been included.

Figure 3. Uranium and bromide breakthrough profiles (uptake phase) for Columns A-D following the conditioning phase of the experiments. Two 12-hour stopped flow events (SFE) are also included. Representative bromide data for Column A are shown with open cross symbols, and closed symbols represent uranium data for columns A-D (1 pore volume (PV) = 3.50 ± 0.25 h). The inset provides a closer view of a stopped flow event for Column D.

Figure 4. Uranium and bromide profiles during both uptake and release phase (observed and fitted using non-equilibrium CDE) for Column B (a) and Column D (b). The release phase of Column D (with phosphate) was not included for uranium fitting because reactions other than adsorption-desorption were likely occurring. Symbols represent the normalized concentrations for bromide and uranium as a function of flow in pore volumes. Dashed and solid lines represent fitted profiles for uranium and bromide respectively.

Figure 5. Sequential extraction results for uranium extracted from three depth increments of Column A, B and D. Results of Background sediments are shown for reference. Error bars represent standard error for the data obtained through duplicate samples.

603 **Figure 6.** Uranium release profiles from Columns B-D following the end of the uptake mode.
604 SRGW with (Columns C-D) or without (Column B) phosphate was started at ~ 353 hours
605 (vertical black dashed line). Stopped flow events (SFE) of 12 hours are also shown. Column C
606 was stopped and sampled after 2 PVs of phosphate-treatment (7.5 h). Closed symbols represent
607 uranium data from different columns (1 PV = 3.5 ± 0.25 h). The inset shows the stopped flow
608 events for Column B.

609 **Figure 7.** Fluorescence spectra of samples obtained from different depths within the columns.
610 Inlet, midsection, and outlet represent samples obtained from different portions of the columns.
611 Spectra of metaschoepite, chernikovite and sodium autunite reference materials are included for
612 comparison.

Table 1. Composition of the Synthetic Rifle Ground Water

Analyte	Concentration (mM)
Na	11.00
Ca	5.00
Mg	4.94
K	0.33
U(VI) ^a	0/4×10 ⁻³
Li ^b	0.13
DIC ^c	7.44
SO ₄	10.78
Cl	3.00
NO ₃	0.53
Si(OH) ₄	0.28
PO ₄ ^a	0/1.00
Br ^b	0.13
pH	7.10

^a Concentration of 0 corresponds to experimental conditions without any addition of U(VI) or PO₄³⁻ in the influent feed

^b Lithium (Li) and bromide (Br) were added as conservative tracers with the influent to aid in the calculation of transport parameters.

^c DIC stands for dissolved inorganic carbon

Table 2. Steps in the sequential extraction method

Step	Target phase	Extractant composition	pH	Procedure
1	Water soluble	Ultrapure water	5.5	Shake suspension 16 h.
2	Ion exchangeable	1 M ammonium acetate	7.0	Shake suspension 16 h. Rinse with ultrapure water.
3	Acid soluble/Carbonate	1 M acetic acid	5.0 ^a	Shake suspension 16 h. Rinse with ultrapure water.
4	Residual solids	8 mL HNO ₃ acid + 2 mL HCl acid + 40 mL DI water	--	Digest in heated block held at 100°C for 4 h.

^a Sodium hydroxide was added to acetic acid solution to raise the pH levels to 5.0.

Table 3. Uranium concentrations in the sediments calculated using mass balance approach

Mass of U ($\mu\text{g/g}$) ¹	Col. A	Col. B	Col. C	Col. D
Released during conditioning phase	0.21 $\pm$ 0.02	0.20 $\pm$ 0.01	0.21 $\pm$ 0.01	0.18 $\pm$ 0.01
Adsorbed during uptake phase	1.90 $\pm$ 0.13	1.68 $\pm$ 0.12	1.69 $\pm$ 0.12	1.98 $\pm$ 0.14
Desorbed during release phase	--	1.95 $\pm$ 0.14	--	0.47 $\pm$ 0.03
Retained or Accumulated	--	-0.27 $\pm$ 0.18 ²	--	1.51 $\pm$ 0.14

¹ Uncertainty estimates come from the propagation of uncertainty in the summation of multiple influent and effluent samples (equation 8) used to estimate the total U amounts taken up or released.

² The number (negative concentration) is statistically not significantly different from zero.

Figure 1. Experimental modes of operation to study the transport of U(VI) through sediments amended with phosphate to induce *in situ* uranium immobilization.

Figure 2. Equilibrium uranium sorption on Rifle sediments (250 g/L) after 2 days of reaction with SRGW for three phosphate concentrations. Trendline(s) included for different starting phosphate concentrations were used to determine K_d values of 0.4, 0.6 and 2.2 mL/g for 0, 100, and 1000 µM P respectively. Only data points for which uranium uptake can be unambiguously assigned to adsorption have been included.

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