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Rate-Limited U(VI) Desorption during a Small-Scale Tracer Test in a Heterogeneous Uranium Contaminated Aquifer

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**Abstract**

A tracer test was performed at the Rifle Integrated Field Research Challenge (IFRC) site to assess the effect of addition of bicarbonate on U(VI) desorption from contaminated sediments in the aquifer and to compare equilibrium and rate-limited reactive transport model descriptions of mass transfer limitations on desorption. The tracer test consisted of injection of a 37 mM NaHCO₃ solution containing conservative tracers followed by downgradient sampling of groundwater at various elevations and distances from the point of injection. Breakthrough curves show that dissolved U(VI) concentrations increased 1.2-2.6 fold above background levels, resulting from increases in bicarbonate alkalinity (from injectate solution) and Ca concentrations (from cation exchange). In general, more U(VI) was mobilized in shallower zones of the aquifer, where finer-grained sediments and higher solid phase U content were found compared to deeper zones. An equilibrium-based reactive transport model incorporating a laboratory-based surface complexation model derived from the same location predicted the general trends in dissolved U(VI) during the tracer test, but greatly overpredicted the concentrations of U(VI), indicating that the system was not at equilibrium. Inclusion of a multi-rate mass transfer model successfully simulated the non-equilibrium desorption behavior of U(VI). Local sediment properties such as sediment texture (weight percent <2 mm), surface area, cation exchange capacity, and adsorbed U(VI) were heterogeneous at the meter scale, and it was important to incorporate these values into model parameters in order to produce accurate simulations.
1. Introduction

Uranium (U) contamination in the subsurface is a part of the legacy of nuclear weapons and energy production, resulting from mining and milling activities, processing of nuclear materials, and nuclear waste disposal. The U.S. Department of Energy (DOE) is tasked with cleaning up U-contaminated aquifers at a number of sites throughout the country, including the Uranium Mill Tailings Remedial Action (UMTRA) sites and the Savannah River, Oak Ridge, and Hanford sites where a variety of different radionuclides are present. Effective remediation of U-contaminated systems requires a detailed understanding of aqueous-phase transport and geochemical behavior. Much of the contamination at the UMTRA sites lies within shallow alluvial aquifers, where U is commonly present in the oxidized U(VI) form at concentrations below the solubilities of U(VI) mineral phases. In these cases, adsorption to mineral surfaces exerts the strongest limitation on U(VI) transport. Many reactive transport models that use a constant distribution coefficient ($K_D$) to describe U(VI) adsorption to aquifer sediments have underpredicted the amount of time required for groundwater U(VI) concentrations to decrease below the maximum contaminant level (MCL) of 0.126 μM [Yabusaki et al., 2008]. Due to the complex aqueous speciation of U(VI) and its effect on U(VI) adsorption, this result is not surprising [Curtis et al., 2009; Curtis et al., 2006]. $K_D$ values for U(VI) sorption onto sediments may vary over several orders of magnitude under environmentally relevant geochemical conditions [Davis et al., 2004].

U(VI) adsorption varies as a function of pH, bicarbonate, and Ca concentrations due to changes in U(VI) aqueous speciation. At moderate bicarbonate concentrations (>1 mM) above pH 7, U(VI) speciation is dominated by uranyl-carbonato complexes
\[ \text{[UO}_2\text{CO}_3(aq), \text{UO}_2(\text{CO}_3)_2^{2-}, \text{UO}_2(\text{CO}_3)_3^{4-}] \text{ in the absence of Ca, and calcium-uranyl-carbonato ternary complexes } [\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0(aq), \text{CaUO}_2(\text{CO}_3)_3^{2-}] \text{ in the presence of typical groundwater Ca concentrations (> 1 mM)} \] [Fox et al., 2006; Dong and Brooks, 2006; Guillaumont et al., 2003]. These calcium-uranyl-carbonato complexes adsorb weakly or not at all to sediments, and thus changes in U(VI) speciation have a large impact on its sorption behavior and transport [Fox et al., 2006; Stewart et al., 2010]. Surface complexation models (SCM) have been successfully used as alternatives to constant \( K_D \) models to describe U(VI) equilibrium adsorption on sediments [Bond et al., 2008; Davis et al., 2004; Hyun et al., 2009] and minerals [Fox et al., 2006; Waite et al., 1994]. Due to its relative simplicity, the generalized composite SCM approach [Davis et al., 2004] lends itself to inclusion in reactive transport models for prediction of contaminant transport in the field [Curtis et al., 2006; Fang et al., 2009; Kent et al., 2000; Yabusaki et al., 2007].

Although equilibrium U(VI) sorption behavior is fairly well understood, natural systems rarely exist in an equilibrium state and inclusion of SCM’s in reactive transport models with a local chemical equilibrium assumption is complicated by a number of factors, such as diffusion constraints on adsorption and desorption from immobile water in small pores and subsurface geochemical and lithological heterogeneity. For example, at the Hanford 300A site in Washington state (USA), non-equilibrium transport of U(VI) appears to be important, perhaps in part because the groundwater velocity is high and groundwater residence times are not long enough for diffusive equilibrium to be reached [Liu et al., 2009; Ma et al., 2010; Qafoku et al., 2005; Yabusaki et al., 2008]. Chemical kinetics for surface complexation reactions at mineral surfaces are generally very fast,
achieving equilibrium in seconds to minutes in the absence of diffusional constraints other than thin film diffusion [Grossl et al., 1997; Hachiya et al., 1984]. Qafoku et al. [2005] applied a multi-rate, linear sorption model to describe the non-equilibrium adsorption/desorption of U(VI) observed in Hanford sediment column experiments. A distributed-rate model employs a distribution of 1st-order rates to describe diffusion processes [e.g., Greskowiak et al., 2011; Haggerty and Gorelick, 1995; 1998; Haggerty et al., 2000; Hay et al., 2011]. However, the Qafoku et al. [2005] model used a linear sorption model, whereas U(VI) sorption is known to be highly non-linear when U(VI) aqueous speciation varies due to changing chemical conditions [Davis et al., 2004].

More recently, Liu et al. [2008] and Greskowiak et al. [2011] substituted the linear sorption term in the multi-rate model with surface complexation reactions, successfully demonstrating an approach for studying non-equilibrium U(VI) adsorption/desorption under variable chemical conditions.

Non-equilibrium sorption behavior of U(VI) is particularly evident in systems undergoing temporal changes in geochemical conditions. Such changes may occur within groundwater plumes during natural attenuation [Curtis et al., 2006; Yabusaki et al., 2008]. Even more rapid geochemical changes occur during active remediation, including remediation by biostimulation [Williams et al., 2011; Yabusaki et al., 2007]. During field bioremediation experiments at the Rifle site, high concentrations of bicarbonate [more than 30 milliequivalents per liter (meq/L)] have been observed, produced by bacterial oxidation of acetate [Fang et al., 2009; Williams et al., 2011; Yabusaki et al., 2007]. In order to create accurate reactive transport models that describe the outcomes of bioremediation experiments, it is necessary to understand the effect of highly variable
bicarbonate concentrations on U(VI) desorption kinetics and mobility under field conditions.

The objectives of this research are to assess the degree and time dependence of U(VI) mobilization following bicarbonate addition to groundwater at the Old Rifle UMTRA site and to compare field scale reactive transport models for equilibrium and rate-limited U(VI) desorption by incorporating a laboratory-based SCM developed by Hyun et al. [2009] for the Rifle field site. An additional objective is to investigate the impact of heterogeneity at the meter scale on U(VI) transport. Field experiments were conducted at the Rifle Integrated Field Research Challenge (IFRC) site as a component of a larger DOE-sponsored project (Rifle IFRC; http://ifcrifle.pnnl.gov) that is focused on gaining an improved mechanistic understanding of U mobility in the subsurface and the use of bioremediation to achieve groundwater U(VI) concentrations below the MCL. In this paper we present the results of a field experiment in which a 37 mM NaHCO$_3$ solution with two non-reactive tracers [bromide ion (Br) and deuterated water ($^2$H$_2$O)] was injected as a pulse into the shallow aquifer at the Rifle site. Using the non-reactive tracers to describe one-dimensional advection and dispersion, we then compare predicted U(VI) desorption and transport with the field observations, using both equilibrium and rate-limited modeling approaches.

2. Materials and Methods

2.1 Site Description

The Old Rifle field site is an UMTRA site located in Rifle, CO on a floodplain of the Colorado River (Figure 1). From 1924-1958 uranium and vanadium ore processing facilities were located on the site and produced mill tailings that were originally disposed
of on site. Remediation of the site was performed from 1992-1996, with removal of mill tailings and contaminated surface soils. However, U contaminated aquifer sediments remained in the vadose and saturated zones, resulting in elevated U(VI) concentrations (0.2-1.2 μM) presently observed in groundwater. Groundwater at the site flows through unconsolidated Quaternary floodplain deposits composed mainly of quartz and feldspar sands, plus silts, clays, pebbles, and cobbles, often coated with iron oxide minerals [DOE, 1999; Hyun et al., 2009; Komlos et al., 2008]. A relatively impermeable bedrock layer at a depth of approximately 8 m is part of the Tertiary Wasatch Formation. Detailed geological and hydrological information about the site is available elsewhere [DOE, 1999].

An array of observation wells designated as Experimental Plot B was installed at the Old Rifle field site as shown in Figure 1. The mean surface elevation at Plot B is 1619.73 m above mean sea level (MSL) with a range of ±0.06 m among all observation wells. The plot location was chosen for its relatively oxidizing conditions and distance from areas of the site used for biostimulation experiments (Plots A and C, Fig. 1). Observation wells include four 10.2 cm diameter wells screened over a 3 m interval in the saturated zone of the aquifer and 21 multi-level sampling (MLS) wells. Solinst Continuous Multichannel Tubing™ (CMT™) was used to construct MLS wells with sampling ports at 3.66, 4.57, 5.49, 6.40, 7.32, and 7.62 m below ground surface (bgs). A diagram of the MLS construction is shown in Figure 2. Groundwater levels at Experimental Plot B vary from 3.20-4.73 m bgs throughout the year, fluctuating as a function of discharge in the adjacent Colorado River. The CMT™ was strapped to 2.54 cm PVC tubing in order to hold the CMT™ rigid while simultaneously providing a larger
diameter sampling port for water level measurements. Each sampling port was hydraulically separated by the emplacement of annular seals between each port using alternating lifts of sand and bentonite pellets during well installation. This multi-level well design allows for groundwater sampling at discrete depths without cross-contamination between sampling depths.

2.2 Sediment Sampling and Analysis

During borehole drilling and installation of the observations wells, aquifer sediments were collected using a 10.2 cm core barrel while purging the borehole with nitrogen. Lithological logs including descriptions of soil texture for each core were recorded and are publicly available on the internet at http://gems.lm.doe.gov. Subsamples of the sediment core were sampled anaerobically, with care taken to prevent oxidation. Immediately after cores were brought to the surface, anaerobic sediment samples were collected in Mylar bags under an N₂ atmosphere, oxygen-absorbing sachets were placed inside the bags, and the bags were sealed and frozen. Frozen samples were shipped to the laboratory on dry ice and stored in a freezer until samples could be analyzed.

Anoxic and oxic carbonate extractions were performed on duplicate sediment samples to estimate the U(IV) and adsorbed U(VI) contents. Anaerobic sediment samples were thawed in an anaerobic glove bag under a 3 % H₂, 97 % N₂, 400 ppm CO₂ atmosphere. A fraction of the sediment was removed from the glove bag and allowed to dry and oxidize in air. Carbonate extractions were then performed on the anaerobic (field-wet) and air-dried sediments. Approximately 10 g of sediment was mixed with 100 mL of carbonate extracting solution (0.4 M Na₂CO₃, 0.093 M NaHCO₃, pH 10.2) in
equilibrium with 400 ppm CO₂/balance N₂ (anoxic) or lab air (oxic). Anoxic extractions were performed in serum bottles. Solution samples were collected at 1 day, 4 weeks, and 7 weeks and analyzed for dissolved U by kinetic phosphorescence analysis (KPA). It was assumed that dissolved U(IV) was insignificant in the anoxic extracts, and thus the U(IV) content of the sediment was estimated by subtracting the U(VI) measured in the anoxic extraction from the dissolved U in the oxic extraction.

Two cores were chosen for more thorough analyses (LR-27 and LR-28; locations shown in Figure 1), including particle size analysis by sieving in the field and laboratory. The core samples were divided into 4-5 depth intervals based on lithological trends and sieved to <38 mm in the field. The <38 mm sediment was homogenized for each depth interval and 1.2-2.5 kg was subsampled and shipped to the laboratory where it was air-dried and sieved to <2 mm. The air–dried <2 mm fraction was analyzed for surface area by BET N₂-adsorption on triplicate samples (2.5 g each), adsorbed U(VI) content by carbonate extraction on duplicate samples (10 g each), and total U by gamma-spectroscopy [Kohler et al., 2004]. The carbonate extraction was performed at a solid-liquid ratio of 50 g/L in a solution of 0.02 M NaCO₃-NaHCO₃ buffered at a pH of 9.4 [Kohler et al., 2004]. Solution samples were collected at various time points for up to 7 weeks and U(VI) was measured in the solution by KPA. Total U was determined on approximately 6 g samples by measurement of the 63 keV line of ²³⁴Th in secular equilibrium with ²³⁸U [Kohler et al., 2004]. Samples were counted until the relative counting error was <10 %. The <2 mm sediment fraction was also analyzed for easily reducible Fe content by hydroxylamine hydrochloride extraction on triplicate samples (5 g each) [Chao and Zhou, 1983]. Air-dried sediment was mixed with 0.25 M
hydroxylamine hydrochloride in 0.25 M hydrochloric acid at a solid-liquid ratio of 200 g/L, heated to 50°C in a shaking water bath and sampled at 0.5 and 96 hr. The 0.5 hr extraction has been shown to represent the amorphous Fe oxide coatings in sediments, while the 96 hr extraction represents the entire pool of easily reducible Fe along with Fe(II) minerals [Chao and Zhou, 1983]. All data is reported as the average of replicate extractions, with standard deviations reported as errors. Solution samples were diluted in 1% nitric acid and analyzed for total Fe by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.3 Groundwater Sampling and Analysis

Groundwater was pumped from each port using a peristaltic pump, with purge volumes of 0.2, 0.2, 0.55, 0.85, 1.2, and 1.2 L for ports at 3.66, 4.57, 5.49, 6.40, 7.32, and 7.62 m bgs, respectively. Purge volumes were calculated by multiplying the volume of standing water in each port by three. Unfiltered groundwater samples were collected for pH, dissolved oxygen, and Fe(II) measurement in the field and filtered (0.45 μm) samples were collected for laboratory analysis. Dissolved oxygen (DO) and Fe(II) were measured using CHEMetrics vacu-vials (chemets) which utilize colorimetric procedures to detect DO (Rhodazine D™) and Fe(II) (phenanthroline). In the laboratory, Br was measured by a colorimetric flow injection analytical (FIA) procedure using a Lachat FIA (Hach Instruments), alkalinity was measured by gran titration with sulfuric acid, U(VI) was measured by KPA (Chemchek Instruments), and other elements (Ca, Mg, K, Na, Fe, Mn, S) were measured by ICP-AES (Thermo Scientific). Samples for KPA and ICP-AES analysis were preserved by acidification to pH 2 in the field with trace metal grade nitric acid. In order to correct for precipitation of calcite in the alkalinity samples, which
occurred as the samples degassed during laboratory storage, the samples were first
titrated to pH 4.5 in the original sample bottles, mixed well, and then allowed to sit for
>24 hours before continuing the titration. A pH increase during the 24-hr period
indicated the presence of carbonate precipitates in the sample and testing verified that this
two-step titration method was sufficient to re-dissolve carbonate precipitates before
completing the titration in step two. The resulting Gran titration plots were linear over
the pH range of 3.0-4.0.

The hydrogen isotopic compositions of water samples were measured by converting
the water to hydrogen gas in a Cr reduction furnace and analysis of the \( ^2\text{H}/\text{H} \) ratio of the
resulting \( \text{H}_2 \) in continuous flow mode with a Micromass Isoprime mass spectrometer.
Breakthrough curves for deuterium were calculated by converting the measured \( \delta^2\text{H} \)
values for the samples into \( ^2\text{H} /\text{H} \) ratios using the following formula consistent with the
definition of delta values:

\[
(\frac{^2\text{H}}{\text{H}})_{\text{sample}} = \left[\frac{(\delta^2\text{H})_{\text{sample}}}{1000} + 1\right] \times (\frac{^2\text{H}}{\text{H}})_{\text{VSMOW}}
\]  

(1)

where \( (\frac{^2\text{H}}{\text{H}})_{\text{VSMOW}} \) has the value 0.000156. The concentration of \( ^2\text{H} \) (in ppm) in the
water was then determined from \( (\frac{^2\text{H}}{\text{H}})_{\text{sample}} \). \( C/C_0 \) values for \( ^2\text{H} \) were calculated using
the following formula:

\[
\frac{C}{C_0} = \frac{(\text{ppm} \ ^2\text{H})_{\text{sample}} - (\text{ppm} \ ^2\text{H})_{\text{background}}}{(\text{ppm} \ ^2\text{H})_{\text{injectate}} - (\text{ppm} \ ^2\text{H})_{\text{background}}}
\]  

(2)

with a background concentration of 137.90 ppm \( ^2\text{H} \) (corresponding to a \( \delta^2\text{H} \) value of -116
\%o based on the average hydrogen isotopic composition measured for pre-injection
groundwater samples) and an initial tracer concentration of 365.82 ppm \( ^2\text{H} \) (from an
average \( \delta^2\text{H} \) value of 1345 \%o for the injectate solution). Given the uncertainties in the
data collection and the initial isotopic compositions of the pore water and injectate solution, the maximum error in the C/C₀ values is estimated to be <0.01.

2.4 Tracer Test

The U(VI) desorption tracer test was performed by injecting 1130 L of water with high bicarbonate concentration into the aquifer on 19 September 2008. Tracer compounds (NaBr, NaHCO₃, deuterated water) were mixed into approximately 100 L of chlorine-free drinking water (Mountain Clear Water Company, Rifle, CO) and allowed to dissolve overnight. The tracers were then transferred to the main tank containing approximately 1030 L of chlorine-free drinking water and mixed well. The water in the tank was re-circulated with 4 water pumps and periodically mixed with a paddle for 4 hours to ensure even distribution of tracers. The injectate water was bubbled with a gas mixture containing 12 % CO₂ and 88 % N₂ for 17 hr in order to achieve a pH of 7.4 and to decrease dissolved oxygen content. The final composition of the injectate solution is shown in Table 1. The injectate solution was injected simultaneously into 2 adjacent MLS wells (LR-MLS-12 and -13, shown in Figure 1) at 3 elevations (5.49, 6.40, and 7.32 m bgs) over 4.2 hours. At the beginning of the injection DO in the injectate was over the maximum value measurable with the chemets (> 44 μM), but decreased to 9.1 μM by the end of the injection. All other constituents remained constant throughout the injection. Groundwater samples were collected from MLS wells at distances of 1.4, 3.0, and 4.5 m downgradient from the injection (LR-MLS-17, -21, and -25, respectively) as a function of time after the injection (Figure 1).

2.5 Reactive transport modeling
Breakthrough curves were simulated using 1-dimensional (1-D) advection-dispersion models that included a Rifle site-specific (<2 mm sediment-based) ion exchange model (including Na, Ca, Mg, K, and H) and the U(VI) surface complexation model described by Hyun et al. [2009]; see reactions and constants in Table 2. The SCM of Hyun et al. [2009] was developed from batch data for two Rifle sediments with very similar properties, a background sediment (BKG-A) collected approximately 1 mile upstream of the Rifle site and a Plot B composite sediment (LRC) collected at the site of the current study; exact locations of the sediments collected are shown in Figure S1 of Hyun et al. [2009]. The authors tested the SCM on core samples from LR-27 and were able to predict U(VI) adsorption on the field materials quite well [Hyun et al., 2009; Supporting Information]. The ion exchange model used in this study was developed on the <2 mm sediment composite from Experimental Plot B (LRC) (P. Fox, unpublished data) and ion exchange coefficients are shown in Table 3. Cation exchange capacity (CEC) and U(VI) sorption site concentrations, known on a <2 mm sediment surface area basis, were converted to effective aqueous concentrations using the <2 mm surface area and mass fraction estimates obtained from well cores, a porosity of 0.25, and an assumed mineral density of 2.65 kg/L. The conversion to U(VI) sorption site densities from calculated surface area was 3.84 µmoles/m², consistent with the SCM. It was assumed that the >2 mm size fraction does not contribute to U(VI) sorption, as has been commonly assumed in other studies [Curtis et al., 2006; Kaplan et al., 2000; Yabusaki et al., 2008]. Although a porosity of 0.27 has been used for previous Rifle modeling [Fang et al., 2009; Yabusaki et al., 2007], the porosity generally varies from 0.2 to 0.3 at the site, with 0.25 representing a reasonable average value. The modeling domain for each breakthrough
curve spanned from the center of the two injection wells to the sampling point and assumed uniform horizontal flow. Groundwater velocities ($v$) and dispersion coefficients ($D$) were obtained by model fitting of the bromide curves, and the mass of bromide in each breakthrough curve (first temporal moment) was simulated by varying the effective injection duration. This approach adjusts for simplification of the transport problem to 1-D even though there are subsurface heterogeneities that affect flow, and has been used in a large number of 1-D reactive transport models for small-scale tracer tests in the literature [e.g., Fang et al., 2009; Friedly et al., 2002; Kent et al., 2007; Kent et al., 2008; Kent et al., 2000; Yabusaki et al., 2007]. A 1-D model is the best approximation for such studies because the spatial resolution of the data is insufficient in the directions perpendicular to flow. The reactive transport model was implemented in PHREEQC [Parkhurst and Appelo, 1999], and least-squares model fitting was performed by iteration of the PHREEQC model using UCODE [Poeter et al., 2005]. Bromide data points were weighted in the UCODE fittings by the inverse of their respective measurement standard deviations, calculated based on duplicate Br analyses.

Transport was described using both equilibrium and non-equilibrium approaches. Non-equilibrium transport was described using a distributed-rate first-order “physical” (i.e. explicit mobile zone/immobile zone) mass transfer model with a lognormal distribution of mass transfer rate constants to approximate diffusion limitations within grain fractures, aggregates, or other non-advective zones. Implementation of the physical mass transfer model with surface complexation is described in detail in Greskowiak, et al. [2011]. Briefly, equilibrium surface complexation reactions are assumed to occur in a non-advective immobile zone, with U(VI) sorption kinetics controlled by mass transfer
between advective and immobile zones. The immobile zone is subdivided into a series of domains, yielding the following equations:

\[
\theta_m \frac{\partial C_m}{\partial t} + \sum_{j=1}^{N} \left( \theta_{im,j} \frac{\partial C_{im,j}}{\partial t} + \rho_b \frac{\partial S_{im,j}}{\partial t} \right) = \theta_m D \frac{\partial^2 C_m}{\partial x^2} - \theta_m \nu \frac{\partial C_m}{\partial x} \tag{3}
\]

\[
\theta_{im,j} \frac{\partial C_{im,j}}{\partial t} + \rho_b \frac{\partial S_{im,j}}{\partial t} = \alpha_j \theta_{im,j} \left( C_m - C_{im,j} \right) \tag{4}
\]

where \( C \) is aqueous concentration, \( \theta \) is porosity, \( S \) is solid-phase (adsorbed) concentration (controlled in this case by surface complexation reactions), \( D \) is the dispersion coefficient, \( \nu \) is the groundwater velocity, \( \alpha_j \) is the mass transfer coefficient for immobile subdomain \( j \), \( \rho_b \) is the bulk density, and the subscripts \( m \) and \( im,j \) denote the mobile zone and \( j^{th} \) immobile domain, respectively. The mass transfer model was applied to the transport of all aqueous components. All surface complexation sites were placed in the immobile zone, distributed uniformly across immobile subdomains, while ion exchange sites were retained in the mobile zone. The initial mobile zone U(VI) concentration was assigned based on observed aqueous U(VI) values, and the immobile zone concentration (aqueous plus sorbed) was based on carbonate extractable U(VI). Each immobile subdomain was assigned uniform volume, with total immobile pore volume assumed to be 3% of the < 2 mm sediment volume, a reasonable value for sediments of this type [Hay et al., 2011]. Note that because the immobile volume is small in this case, its effect on the transport of conservative components is small. Because a large fraction of the surface area may be associated with this type of intragranular, immobile porosity [Hay et al., 2011], it can simultaneously have a large effect on the transport of adsorbing species such as U(VI) and a negligible effect on non-sorbing species [Greskowiak et al., 2011].
Values of $\alpha_j$ were determined by uniform discretization of the cumulative lognormal distribution function

$$cdf(\alpha; \mu, \sigma) = \frac{1}{2} + \frac{1}{2} \text{erf} \left( \frac{\ln(\alpha) - \mu}{\sigma \sqrt{2}} \right)$$

(5)

where $\mu$ and $\sigma$ are the mean and standard deviation of the lognormal distribution describing $\alpha$. Mixing factors required for implementation of the mass transfer model in PHREEQC were calculated from $\alpha_j$ according to equations provided in the PHREEQC manual [Parkhurst and Appelo, 1999]. A minimum $N$ value of 20 was used in the discretization to approximate a continuous distribution.

Optimized $\mu$ values were determined by model fitting using UCODE. Uranium data in the peak region were weighted in the fitting by the inverse of the KPA measurement standard deviation. This is the standard deviation calculated by the KPA instrument based on multiple fluorescence decay measurements on a single sample, which was consistently found to be greater than the standard deviation between sample duplicates. To focus the fitting on the uranium concentration peak, data points within $\pm 10\%$ of the ambient groundwater U(VI) concentration were given negligible weight. A high degree of correlation was observed when both $\mu$ and $\sigma$ were allowed to vary in the fitting, such that large changes in $\mu$ could be compensated by changing $\sigma$ without much change in the ultimate model fit. Thus, to obtain a set of optimized $\mu$ values that could be meaningfully compared across wells, $\sigma$ was held at a constant value. Results are given for $\sigma = 2.0$ (in units of $\ln(\text{hr}^{-1}))$, which was chosen by varying $\sigma$ systematically between 0.5 and 3 and finding the value that provided the best overall fit for most wells after
reoptimization of $\mu$. More detail on the choice of $\sigma$, including a sensitivity analysis with varying $\sigma$, is provided in Appendix A.

3. **Results and Discussion**

3.1 *Characterization of Alluvial Sediment and Groundwater Samples*

Tables 4 and 5 show the particle size distribution, surface area, total U, and bicarbonate extractable U and Fe as a function of depth in two cores collected from Plot B. While the shallower sediments have a larger fraction of gravels (2-64 mm) and cobbles (64-256 mm), the <2 mm fraction of the sediment transitions from silt-dominated to sand-dominated with depth, as evidenced by the decrease in surface area of the < 2mm fraction with depth. This general lithological trend was observed in most of the cores collected from Plot B, although the exact depth at which the transition occurs varies, ranging from 4.3 to 6.1 m bgs. Lithological logs from these cores are available on the internet at http://gems.lm.doe.gov. While a similar range of sediment properties has been observed at other locations at the Rifle site, i.e. in Plot A [Yabusaki et al., 2011] this particular vertical lithologic trend has not been observed at other locations. Several thin clay zones were also observed in the cores, predominantly in the shallower zones of the aquifer. The largest clay zone encountered was approximately 15.2 cm thick and located in well LR-10 at approximately 6.40 m bgs. Carbonate-extractable U(VI) and U(IV) contents in sediments collected during installation of the wells (from oxic and anoxic carbonate extractions) are shown in Table 6. The only sample in which U(IV) was detected was the clay layer at 6.40 m bgs in LR-10, accounting for approximately 28% of the total carbonate extractable U content in the sample. Carbonate-extractable U(VI)
contents typically range from 0.3-2.3 nmol/g, but also reach concentrations as high as 8.18 nmol/g (LR-25, 3.96 m bgs) and 20.98 nmol/g (LR-10, clay layer at 6.40 m bgs). The concentration of bicarbonate extractable U(VI) generally decreased with depth, with the highest concentrations occurring near the water table (Tables 5 and 6). When bicarbonate extractable U(VI) concentrations are normalized to surface area instead of to mass, the variation with depth is less pronounced, but still exists.

Pre-injection aqueous geochemical data for the breakthrough MLS wells are shown in Table 1. U(VI) aqueous speciation, calculated from the data in Table 1 and the thermodynamic data in Hyun et al. [2009; references therein], was dominated by the Ca$_2$UO$_2$(CO$_3$)$_3$ and CaUO$_2$(CO$_3$)$_3$$^{2-}$ species, comprising 67.5-74.9 % and 24.2-31.0 % of the total dissolved U(VI), respectively. The highest median dissolved U(VI) concentrations in Plot B were observed near the water table (Figure 3) where the highest sediment U(VI) concentrations were observed. There was also a much greater degree of variation in dissolved U(VI) concentrations across Plot B in the shallower depths, becoming more uniform with depth. This likely reflects similar variations in sediment properties and is in fact consistent with observations of sand and gravel dominated zones at depth. The higher dissolved and solid-phase U concentrations observed near the water table (at 3.2-4.7 m bgs) suggest that this may serve as a zone of accumulation for U(VI).

Although there is a fair amount of spatial heterogeneity, this region of the aquifer can be generally characterized as suboxic. Dissolved oxygen (DO) levels in Plot B were generally very low (<1 μM) or undetectable (<0.2 μM) except near the water table, where values of 2-50 μM were observed. While most ports contain low (1-2 μM) concentrations of dissolved Fe(II), a few sampling points had consistently high Fe(II)
concentrations (50-100 μM). Dissolved Mn concentrations were extremely low at the water table (median of 5.5 \times 10^{-8} \text{ M} at 3.66 \text{ m bgs}), exhibited peak concentrations at 4.57 m bgs (median of 2.5 \times 10^{-5} \text{ M}), and decreased with elevation below that (Figure 3). Under oxic to suboxic conditions, the most stable valence of U is U(VI) \cite{Guillaumont2003}. Even in the presence of Fe(II), U(VI) can still be the stable valence at circumneutral pH and high bicarbonate and Ca concentrations \cite{Ginder-Vogel2008, Ginder-Vogel2006}. While iron oxide-reducing conditions likely were present in a few specific spots, U mobility appeared to be predominantly controlled by U(VI) adsorption-desorption reactions as evidenced by the good agreement between \textit{in situ} and model-predicted $K_D$ values \cite{Hyun2009}.

3.2 U(VI), Br, $^2H$, and Alkalinity Transport during Tracer Test

Breakthrough curves for U(VI), Br, and alkalinity are shown in Figures 4 and 5 for injection MLS and MLS located 1.36, 3.17, and 4.74 m downgradient from the injection at different depths. In all cases, dissolved U(VI) increased as the high alkalinity injectate solution came into contact with sediments, causing desorption of adsorbed U(VI) and increasing U(VI) mobility. Breakthrough curves were very similar at 7.32 and 7.62 m bgs (see Auxiliary Materials for 7.62 m bgs). The total amount of U(VI) desorbed from the sediments at each sampling location can be quantified by calculating the predicted U(VI) concentration at each point along the breakthrough curve based purely on mixing of the injected tracer and native groundwater (estimated from the bromide breakthrough curve), and subtracting that value from the observed U(VI) concentrations. The resulting U(VI) concentration curves can then be integrated over the range of positive values to determine the total amount of U(VI) desorbed during the tracer test.
Table 7 shows both the total U(VI) and total U(VI) divided by the total integrated Br concentration for each of the observation wells. When net integrals are scaled with respect to Br they provide an assessment of the amount of U(VI) desorbed from sediments relative to the amount of tracer observed at each sampling location. There was a large difference in the amount of U(VI) desorbed at 6.40 m bgs compared to 7.32 and 7.62 m bgs which was particularly evident at 1.36 m downgradient (Table 7). This is consistent with higher U contents observed in core samples (Tables 5 and 6). The amount of U(VI) released from the sediments also increased with transport distance for all three depths, indicating that U(VI) desorption may not be at equilibrium.

Groundwater velocities ($v$) and dispersion coefficients ($D$) obtained by model fitting of the bromide breakthrough curves are listed in Table 8. At 6.40 m bgs, groundwater velocity was 0.16 m/day and broad breakthrough curves for Br, U(VI), and alkalinity were observed for well LR-17 (1.36 m downgradient from injection; Figure 5). However, at 7.32 m bgs in LR-17, groundwater velocity was 1.1 m/day. The same trend (higher groundwater velocities at 7.32 and 7.62 m bgs compared to 6.40 m bgs) was observed for well LR-21. This result is consistent with the vertically distributed trends in particle size distribution observed in core samples. Bromide breakthrough curves were well described using the equilibrium advection-dispersion model, with the exception of the lower LR-17 depths (7.32 and 7.62 m bgs). These latter curves exhibited sharp concentration fronts, but the transport model predictions using a dispersion coefficient similar to that found for other wells yielded peak tracer concentrations much higher than observed (results not shown). This is possibly the result of sampling artifacts and proximity to the injection well; for example, in these ports tracer dilution may result from
mixing of different flow channels near the well during sampling, rather than transport-induced mixing which would cause dispersion. Optimum $D$ values could not be achieved within a reasonable range for these two depths, so $D$ was fixed at a relatively high value of 1.2 m$^2$/d and optimizations were rerun for $v$ only.

With increasing transport distance, the observed mean groundwater velocities at 6.40 m bgs appeared to increase, while groundwater velocities at 7.32 and 7.62 m bgs decreased, thus resulting in convergence of calculated groundwater velocities (0.42-0.50 m/day) after 4.74 m of transport for all three well depths (Table 8). This result suggests that particle-tracking flowpaths likely would not follow directly from well LR-17 to wells LR-21 and LR-25 (i.e., each MLS likely sampled different vertical “slices” of the tracer plume), and complex local flow paths likely exist.

Normalized concentration for bromide and deuterium ($^2$H) are plotted versus time for well LR-17 (1.36 m downgradient of the injection) in Figure 6. Generally, the data for the two tracers track each other as expected, but there were some measureable differences in breakthrough curves for the two tracers. For both elevations shown, the $^2$H breakthrough curves appear to be shifted towards slightly later times in comparison to the Br curves, suggesting slower velocities for $^2$H than for Br. This effect is more pronounced in the shallower, finer-grained interval at 6.40 m bgs than at 7.32 m bgs, where $C/C_o$ values for Br were more than 15 % higher for the initial six days of the tracer test. There was little to no difference in optimized $v$ for $^2$H and Br at the two well depths (0.145 m/day, vs. 0.16 m/day for Br at 6.40 m bgs). Due to the very small differences in optimized $v$ between the two tracers we chose to use Br for modeling purposes. Br has the advantage of greater analytical ease and lower analytical cost.
The most likely explanation for the differential behavior of the two tracers is anion exclusion [Gvirtzman and Gorelick, 1991]. Br tracer can be excluded from smaller pore spaces where negatively-charged surfaces of minerals repel the anion. Deuterated water molecules are not affected by this process because they are neutral species that act identically to H₂O. A similar differential behavior was observed by Conrad et al., [2007] for vadose zone tracer tests conducted in sediments at the Hanford site in Washington State. Other possible explanations for the differential behavior of Br and ²H include isotopic exchange of ²H with protons associated with sediments and differential diffusion of ²H and Br, but these effects are believed to be small relative to the observed retardation.

Comparison of the alkalinity breakthrough curves with predictions made using the bromide-calibrated model suggests that the alkalinity plume behaved non-conservatively. In some cases, the peak alkalinity concentrations were lower than predicted (Figure 5), suggesting a reduction of alkalinity due to sediment-water reactions, possibly via production of acid or decrease in bicarbonate concentration due to precipitation. As will be shown below, the Ca data suggest that calcite did not precipitate to a measurable extent. Given the sensitivity of U(VI) adsorption to bicarbonate alkalinity, an overprediction of alkalinity in the model would tend to slightly overestimate desorption of U(VI). However, as will be discussed below, the rate limitation on U(VI) desorption has a far larger impact than the overprediction of alkalinity for some of the breakthrough curves.

3.3 Ion Exchange during Tracer Test
Ion exchange between Na and Ca also influenced the extent of U(VI) desorption from the sediments. As shown in Figure 7, cation exchange between injected Na (from NaBr and NaHCO₃) and exchangeable Ca and Mg resulted in increases in Ca and Mg concentrations above background levels, followed by decreases below background levels corresponding to re-exchange after passing of the tracer plume. Although less clear, this increase in Ca and Mg preceding the decrease is also present in LR-17, 7.32 m bgs, though the peak is condensed due to the high groundwater velocity. Higher Ca concentrations favor U(VI) desorption due to formation of the highly stable aqueous Ca-UO₂-CO₃ ternary complexes [Fox et al., 2006; Stewart et al., 2010]. The increase in dissolved Ca and Mg was greatest in the slow-moving groundwater observed at 6.40 m bgs after 1.36 m of transport, and was coincident with greater U(VI) desorption. Ion exchange was included in the reactive transport model for Na, Ca, Mg, K, and H using ion exchange constants from laboratory batch and column experiments (Table 3). The ion exchange model provided a good prediction of the Na, Ca, and Mg dynamics in most cases, particularly at the 7.32 m bgs depth. Model predictions at 6.40 m bgs were also adequate for the LR-21 and LR-25 breakthrough curves, while the model did not perform as well for LR-17 at this depth, possibly due to an underestimation of the CEC for this location. While CEC (Table 3) was adjusted for each depth based on the mass of sediment <2 mm and the surface area of the <2 mm fraction (Table 8), the CEC was assumed to be constant for a given depth across wells (i.e. constant horizontal lithology). Data and model predictions for the 7.62 m bgs depth wells are included in the Auxiliary Materials along with data showing changes in K, S, Fe, and Mn concentrations.
The dynamics observed in the pH breakthrough curves suggests that ion exchange is an important process affecting pH as well (Figure 8). The model reproduces the general trend observed: a dip in pH resulting from H\(^+\) displacement by Na\(^+\), followed by a pH rebound corresponding to H\(^+\) re-adsorption. The calcite saturation index is plotted along with pH in Figure 8, demonstrating that for the observed alkalinity, pH, and Ca concentrations, the aquifer remains supersaturated with respect to calcite for the duration of the tracer test, with saturation indices approaching 1.0 near the peak of the alkalinity plume. Given the sustained supersaturation observed and the fact that the model predicted the experimentally observed supersaturation levels well without calcite precipitation, calcite was not allowed to precipitate in the transport model. The supersaturation is presumed to result from inhibition of both calcite crystal growth and nucleation via surface poisoning agents such as sulfate, phosphate, and organic matter [e.g., Bischoff and Fyfe, 1968; House, 1987; Inskeep and Bloom, 1986; Meyer, 1984].

3.4 Equilibrium Reactive Transport Modeling of U(VI)

To describe U(VI) desorption and transport, the SCM developed by Hyun et al. [2009] for the <2 mm sediment fraction was included in the equilibrium reactive transport model described above (Table 2). In all cases, the predicted quantity of U(VI) desorbed was considerably greater than that observed. Example equilibrium model predictions are shown in Figure 9 for LR-17 and LR-21 (6.40 m bgs), where the predicted peak U(VI) concentrations are 2.5-5 times greater than the observed peak. Similar results were obtained for the other well depths (see Auxiliary Materials). As distance from the injection well increases and alkalinity concentrations decrease, the predicted U(VI) concentrations also decrease, but still vastly overpredict the observed U(VI)
concentrations. A small part of the overprediction of U(VI) stems from the model overpredictions of alkalinity; reducing the injectate concentrations in the model to reproduce the observed alkalinites only marginally improved the dissolved U(VI) predictions (results not shown). Rather, the discrepancy in magnitude and timing between the observed and predicted U(VI) desorption peaks strongly suggests rate-limited U(VI) desorption.

3.5 Non-Equilibrium Reactive Transport Modeling of U(VI)

To capture the observed sorption non-equilibrium, a multirate mass transfer model with a lognormal distribution of rate coefficients [Greskowiak et al., 2011; Liu et al., 2008] was incorporated into the reactive transport model as described in the methods section. Optimized \( \mu \) values are given in Table 8 for all U(VI) breakthrough curves, and the model fits to the breakthrough curves are shown for the 6.40 and 7.32 m bgs depths in Figure 10. Although the results are also sensitive to changes in \( \theta_m \) and \( \sigma \), there is some correlation between these values and \( \mu \), and the model simulations are not substantially different for reasonable ranges of \( \theta_m \) and \( \sigma \) after re-optimization of \( \mu \) (see Appendix A).

Optimized \( \mu \) ranged from -5.8 to -3.2, resulting in good model fits for most of the breakthrough curves. To gain a better appreciation for these differences in rates, Figure 11 also includes model predictions obtained using an average \( \mu \) of -4.66. The differences in mean rate constant may be indicative of spatial heterogeneities within the aquifer that lead to spatially variable, rate-limited desorption. The overall decrease in \( \mu \) with distance from the injection possibly suggests a scale dependence for the apparent desorption rate (i.e., slower effective desorption rates on larger spatial scales). However, small differences in the optimized rate constant may also reflect cumulative model uncertainty.
For example, we do not expect to obtain an accurate prediction of U(VI) desorption when the alkalinity, Ca, and pH predictions show some discrepancy, though it is easy to compensate for these discrepancies via optimization of $\mu$.

In some cases (e.g., LR-21, 7.32 m bgs), the model yielded a good description of the U(VI) peak, but a poorer description of the concentration rebound corresponding to U(VI) re-adsorption, despite good predictions of pH, alkalinity, and Ca in this region. This may suggest that the total quantity of U(VI) available for desorption has been overestimated based on well core data in these cases, or that the SCM is slightly underpredicting the adsorption strength. While the model takes vertical heterogeneities in sediment properties into account, it does not account for variations between wells, instead assuming an average value for each depth which leads to some uncertainty in the model predictions. The fact that the equilibrium model slightly overpredicts aqueous U(VI) even before the arrival of the tracer plume illustrates that there is some uncertainty in the equilibrium SCM (Figure 9). Regardless, the combined surface complexation/mass transfer approach provides a very good overall description of U(VI) desorption and transport in this system. Similar modeling approaches have been applied to U(VI) transport in laboratory experiments [Liu et al., 2009; Liu et al., 2008; Shang et al., 2011] and at the field scale under background geochemical conditions [Greskowiak et al., 2010; Ma et al., 2010], but to our knowledge, this is the first time it has been successfully applied in a field scenario at the meter scale with large spatial and temporal geochemical gradients. It is clear from the results that both equilibrium and rate-limited model predictions were strongly affected by the variation of sediment properties observed at the meter scale. We have also studied U(VI) desorption in laboratory columns packed
homogeneously with the < 2 mm fraction of Rifle sediment and preliminary modeling suggests that the U(VI) desorption rate is considerably faster in the column experiments. This suggests that sediment heterogeneity in the field experiment contributed to a slower rate of desorption. This is also consistent with the large difference in $\mu$ observed between this study and the laboratory column studies of Liu et al. [2008], where an equivalent physical mass transfer model $\mu$ value of +0.39 was obtained (see Table 2, Greskowiak et al. [2011]). This comparison is only qualitative, however, since those studies were performed on sediments from a different site, with different $\sigma$ and $\theta_m$ values used in the mass transfer model. As mentioned above, $\mu$ and $\sigma$ values were highly correlated, so it is not justified to infer particular significance to the similarity of the $\mu$ values in this study and that of Liu et al. [2008].

4. Conclusions

This study investigated the mobilization of U(VI) through desorption during bicarbonate addition to an alluvial aquifer. Subsurface heterogeneities resulted in large differences in tracer breakthrough curves at different locations and elevations in the study area. Specifically, a slow-moving zone located at 6.40 m bgs near the point of injection resulted in much greater U(VI) desorption than at deeper elevations (7.32 and 7.62 m bgs). This result is consistent with observations of differences in particle size distribution, sediment surface area, and U content as a function of depth in core samples collected in the study area and underscores the importance of subsurface heterogeneities as controls over U(VI) mobility in aquifers. Inclusion of information on subsurface heterogeneities in the reactive transport model was necessary to accurately describe U(VI) sorption and mobility during this test at the meter scale. While the inclusion of a
laboratory-derived SCM can explain the effect of changing aqueous geochemistry (namely bicarbonate and Ca concentrations) on U(VI) mobility under equilibrium conditions, dissolved U(VI) concentrations were greatly overpredicted by an equilibrium-based approach, indicating that U(VI) desorption was rate-limited. Instead, a multi-rate mass transfer model with a log normal distribution of rate coefficients was used to describe U(VI) mobilization, resulting in good descriptions of U(VI) breakthrough curves at most locations. To our knowledge, this is the first time that this rate-limited modeling approach has been used to describe meter-scale, high geochemical gradient field tracer test observations of U(VI) transport. The results suggest that the rapid geochemical changes that occur during bioremediation by biostimulation (e.g. increase in bicarbonate concentration) will have a significant impact on U(VI) aqueous speciation and desorption, and are likely to have an indirect effect on the net rates of U(VI) reduction during biostimulation.

Appendix A.

The variables $\theta_{im}$ and $\sigma$ were held constant at reasonable values in the fitting of the multirate mass transfer model to the U(VI) breakthrough curves, such that optimization proceeded by adjustment of $\mu$ only. For this reason, a sensitivity analysis was performed to illustrate the effects of changes in $\theta_{im}$ and $\sigma$ on model simulations. Figure A1 shows the model results for well LR-21 (6.40 m bgs) when $\theta_{im}$ and $\sigma$ are adjusted +/- 50 % from their original values.

Increasing $\theta_{im}$ from 3% to 4.5% of the < 2 mm sediment volume (Figure A1, first panel) resulted in an increase in U(VI) released for the given value of $\mu$ (gray dotted line), while decreasing this quantity from 3 % to 1.5 % resulted in a decrease in U(VI)
release (gray dashed line). However, these effects could be compensated for by reoptimization of $\mu$, with little overall change in the peak shape (black dashed and dotted lines). Specifically, the increase of $\theta_{im}$ required adjustment of $\mu$ from -5.04 to -5.30, while decreasing $\theta_{im}$ required an adjustment in $\mu$ to -4.53. Thus, for this particular data set, $\theta_{im}$ and $\mu$ exhibit a high degree of correlation, suggesting that the absolute values of $\mu$ hold significance only for a given value of $\theta_{im}$. However, since these effects should be similar for the other breakthrough curves, the variations in $\mu$ as a function of location described in the text hold significance, since a constant $\theta_{im}$ value was used.

Similar effects were observed on adjustment of $\sigma$ (Figure 1A, second panel). When $\sigma$ was increased to 3.0 (widening the rate constant distribution), the U(VI) peak height increased, while decreasing $\sigma$ to 1.0 resulted in a decrease in peak height. This illustrates that the U(VI) response on the timescale of the tracer injection is largely controlled by the faster rates within the distribution, as expected. As with $\theta_{im}$, adjustments in $\sigma$ could be compensated for by reoptimization of $\mu$, with $\mu = -6.15$ for $\sigma = 3.0$ and $\mu = -4.27$ for $\sigma = 1.0$. Unlike $\theta_{im}$, however, adjustments in $\sigma$ have a noticeable effect on the curve shape and timing of the U(VI) peak, and the results demonstrate that the best fit is obtained with a $\sigma$ value near 2.0. Since narrowing the distribution had an adverse effect on the model fit (black dashed line), it is clear that the multirate model performs better than a single rate model would ($\sigma \to 0$).

Acknowledgements
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References


DOE (1999), Final Site Observational Work Plan for the UMTRA project Old Rifle site, Grand Junction, CO.


Table 1. Injection water and background water chemistry for three breakthrough wells (LR-17, LR-21, and LR-25) at 6.40, 7.32, and 7.62 m below ground surface.

<table>
<thead>
<tr>
<th></th>
<th>U(VI) (µM)</th>
<th>Br (mM)</th>
<th>H (ppm)</th>
<th>Alkalinity (meq/L)</th>
<th>pH</th>
<th>Fe²⁺ (µM)</th>
<th>DO³</th>
<th>Ca (mM)</th>
<th>Mg (mM)</th>
<th>Na (mM)</th>
<th>K (mM)</th>
<th>S (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injectate</td>
<td>ND</td>
<td>5.6</td>
<td>382</td>
<td>37</td>
<td>7.45</td>
<td>ND</td>
<td>9 to &gt;44</td>
<td>0.05</td>
<td>0.01</td>
<td>41.2</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>LR-17, 6.4m</td>
<td>0.18</td>
<td>ND</td>
<td>138</td>
<td>7.6</td>
<td>7.31</td>
<td>3.4</td>
<td>ND</td>
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<td>2.03</td>
<td>11.0</td>
<td>0.14</td>
<td>5.31</td>
</tr>
<tr>
<td>LR-17, 7.3m</td>
<td>0.17</td>
<td>ND</td>
<td>138</td>
<td>7.7</td>
<td>7.17</td>
<td>ND</td>
<td>ND</td>
<td>4.06</td>
<td>3.97</td>
<td>5.14</td>
<td>0.14</td>
<td>5.44</td>
</tr>
<tr>
<td>LR-17, 7.6m</td>
<td>0.15</td>
<td>ND</td>
<td>--</td>
<td>7.7</td>
<td>7.20</td>
<td>0.2</td>
<td>ND</td>
<td>3.99</td>
<td>3.88</td>
<td>4.89</td>
<td>0.13</td>
<td>5.26</td>
</tr>
<tr>
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<td>ND</td>
<td>0.21</td>
<td>ND</td>
<td>8.2</td>
<td>7.19</td>
<td>4.7</td>
<td>0.5</td>
<td>4.48</td>
<td>4.27</td>
<td>6.00</td>
<td>0.15</td>
<td>6.23</td>
</tr>
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<td>LR-21, 7.3m</td>
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<td>ND</td>
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<td>7.26</td>
<td>ND</td>
<td>0.6</td>
<td>4.08</td>
<td>3.94</td>
<td>5.01</td>
<td>0.14</td>
<td>5.47</td>
</tr>
<tr>
<td>LR-21, 7.6m</td>
<td>ND</td>
<td>0.15</td>
<td>ND</td>
<td>7.4</td>
<td>7.26</td>
<td>ND</td>
<td>ND</td>
<td>4.02</td>
<td>3.90</td>
<td>4.96</td>
<td>0.14</td>
<td>5.35</td>
</tr>
<tr>
<td>LR-25, 6.4m</td>
<td>ND</td>
<td>0.21</td>
<td>ND</td>
<td>7.8</td>
<td>7.23</td>
<td>7.5</td>
<td>0.3</td>
<td>4.16</td>
<td>3.95</td>
<td>5.92</td>
<td>0.15</td>
<td>5.74</td>
</tr>
<tr>
<td>LR-25, 7.3m</td>
<td>ND</td>
<td>0.19</td>
<td>ND</td>
<td>7.7</td>
<td>7.23</td>
<td>0.2</td>
<td>0.2</td>
<td>4.14</td>
<td>3.94</td>
<td>5.42</td>
<td>0.15</td>
<td>5.57</td>
</tr>
<tr>
<td>LR-25, 7.6m</td>
<td>ND</td>
<td>0.17</td>
<td>ND</td>
<td>8.4</td>
<td>7.20</td>
<td>1.8</td>
<td>5.2</td>
<td>4.12</td>
<td>3.94</td>
<td>5.37</td>
<td>0.15</td>
<td>5.42</td>
</tr>
</tbody>
</table>

³DO=dissolved oxygen
²ND=not detected
³DO varied in the injectate over time, starting at >44 µM and dropping to 9 µM.
⁴not measured
Table 2. Surface complexation constants\(^a\) for U(VI) used in the transport model.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log ( K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S_{i}(\text{OH})<em>{2} + \text{UO}</em>{2}^{2+} = S_{i}(\text{OH},\text{O})\text{UO}_{2}^{+} + \text{H}^{+} )</td>
<td>7.85</td>
</tr>
<tr>
<td>( T_{i}(\text{OH})<em>{2} + \text{UO}</em>{2}^{2+} = T_{i}(\text{OH},\text{O})\text{UO}_{2}^{+} + \text{H}^{+} )</td>
<td>3.46</td>
</tr>
<tr>
<td>( S_{i}(\text{OH})<em>{2} + \text{UO}</em>{2}^{2+} + 2\text{H}<em>{2}\text{CO}</em>{3} = S_{i}(\text{OH},\text{O})\text{UO}<em>{2}(\text{CO}</em>{3})_{2}^{3-} + 5\text{H}^{+} )</td>
<td>-15.21</td>
</tr>
<tr>
<td>( T_{i}(\text{OH})<em>{2} + \text{UO}</em>{2}^{2+} + 2\text{H}<em>{2}\text{CO}</em>{3} = T_{i}(\text{OH},\text{O})\text{UO}<em>{2}(\text{CO}</em>{3})_{2}^{3-} + 5\text{H}^{+} )</td>
<td>-20.03</td>
</tr>
</tbody>
</table>

\(^a\)Log \( K \) values from the model of Hyun et al. (2009), with slight modification to account for data re-calibration to be consistent with the new log \( K \) value (log \( K \) = 25.8) for the aqueous species, \( \text{MgUO}_{2}(\text{CO}_{3})_{3}^{2-} \), given in [Dong and Brooks, 2008]. The original model of [Hyun et al., 2009] was based on the log \( K \) value of 26.1 published in [Dong and Brooks, 2006].

Table 3. Ion exchange constants\(^a\) used in the transport model.

<table>
<thead>
<tr>
<th>CEC (eq/m(^2))</th>
<th>1.14\times10^{-05}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Log ( K )</td>
<td></td>
</tr>
<tr>
<td>Na-Na</td>
<td>0</td>
</tr>
<tr>
<td>Na-Ca</td>
<td>0.9</td>
</tr>
<tr>
<td>Na-Mg</td>
<td>0.8</td>
</tr>
<tr>
<td>Na-K</td>
<td>1.0</td>
</tr>
<tr>
<td>Na-H</td>
<td>4.9</td>
</tr>
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</table>

\(^a\) P. Fox, unpublished data
Table 4. Particle size distribution as a function of depth from core samples (LR-27 and LR-28) collected in Experimental Plot B.

<table>
<thead>
<tr>
<th>Depth (m bgs)</th>
<th>38-102 mm</th>
<th>13-38 mm</th>
<th>2-13 mm</th>
<th>&lt;2 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>LR-27 core</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.74-3.81</td>
<td>29</td>
<td>29</td>
<td>12</td>
<td>31</td>
</tr>
<tr>
<td>3.81-4.57</td>
<td>36</td>
<td>21</td>
<td>14</td>
<td>29</td>
</tr>
<tr>
<td>4.57-5.34</td>
<td>20</td>
<td>25</td>
<td>18</td>
<td>36</td>
</tr>
<tr>
<td>5.34-7.16</td>
<td>12</td>
<td>2</td>
<td>5</td>
<td>80</td>
</tr>
<tr>
<td>7.16-7.77</td>
<td>30</td>
<td>8</td>
<td>5</td>
<td>58</td>
</tr>
</tbody>
</table>

| LR-28 core    |            |           |         |       |
| 2.74-5.33     | 24         | 27        | 16      | 33    |
| 5.33-6.10     | 10         | 18        | 11      | 61    |
| 6.10-7.16     | 27         | 21        | 14      | 39    |
| 7.16-7.92     | 16         | 4         | 11      | 69    |

Table 5. Surface area, hydroxylamine hydrochloride (HH) extractable Fe, carbonate-extractable (labile) U(VI), and total U of the <2 mm fraction of core samples (LR-27 and LR-28) as a function of depth. Errors are standard deviations of replicate samples unless otherwise noted.

<table>
<thead>
<tr>
<th>Depth (m bgs)</th>
<th>Surface Area (m²/g)</th>
<th>Total U (nmol/g)</th>
<th>Labile U(VI) (nmol/g)</th>
<th>Dissolved U(VI) (μM)</th>
<th>0.5 hr HH-Fe (μmol/g)</th>
<th>96 hr HH-Fe (μmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LR-27 core</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.74-3.81</td>
<td>5.0±0.0</td>
<td>14.0±2.2</td>
<td>0.75±0.02</td>
<td>0.43</td>
<td>4.77±0.41</td>
<td>54.4±4.4</td>
</tr>
<tr>
<td>3.81-4.57</td>
<td>4.9±0.2</td>
<td>20.3±3.7</td>
<td>2.27±0.03</td>
<td>0.36</td>
<td>5.69±0.24</td>
<td>40.3±0.8</td>
</tr>
<tr>
<td>4.57-5.34</td>
<td>4.5±0.1</td>
<td>14.3±2.7</td>
<td>1.06±0.02</td>
<td>0.16</td>
<td>6.98±0.77</td>
<td>41.8±3.5</td>
</tr>
<tr>
<td>5.34-7.16</td>
<td>3.3±0.2</td>
<td>13.5±2.1</td>
<td>0.49±0.01</td>
<td>0.19</td>
<td>4.21±0.26</td>
<td>71.6±1.4</td>
</tr>
<tr>
<td>7.16-7.77</td>
<td>2.6±0.1</td>
<td>10.5±1.5</td>
<td>0.28±0.01</td>
<td>0.18</td>
<td>4.08±0.80</td>
<td>64.9±2.9</td>
</tr>
</tbody>
</table>

| LR-28 core    |                     |                  |                       |                      |                       |                       |
| 2.74-5.33     | 4.9±0.3             | --               | 1.09±0.02             | --                   | --                    | --                    |
| 5.33-6.10     | 2.4±0.1             | --               | 0.39±0.01             | 0.24                 | --                    | --                    |
| 6.10-7.16     | 2.1±0.0             | --               | 0.34±0.00             | 0.21                 | --                    | --                    |
| 7.16-7.92     | 2.1±0.1             | --               | 0.35±0.03             | 0.18                 | --                    | --                    |

*Samples were collected for dissolved U(VI) measurement from LR-27 at depths of 3.66, 4.57, 5.49, 6.40, and 7.32 m bgs and from LR-28 at 5.49, 6.40, and 7.32 m bgs on May 31, 2009.

*Errors for Total U measurements represent counting errors for a single sample.

*Not measured
Table 6. Carbonate extractable U(VI) and U(IV) content of sediment collected from wells in the tracer test area as determined by anoxic-oxic carbonate extractions. Errors are standard deviations of duplicate samples.

<table>
<thead>
<tr>
<th>Depth (m bgs)</th>
<th>U(IV) content (nmol/g)</th>
<th>U(VI) content (nmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.40 m (clay layer)</td>
<td>8.12±0.89</td>
<td>20.98±0.17</td>
</tr>
<tr>
<td>LR-10</td>
<td>3.96</td>
<td>nd^a</td>
</tr>
<tr>
<td>LR-17</td>
<td>4.88</td>
<td>nd</td>
</tr>
<tr>
<td>LR-21</td>
<td>5.79</td>
<td>nd</td>
</tr>
<tr>
<td>LR-25</td>
<td>7.01</td>
<td>nd</td>
</tr>
</tbody>
</table>

^a nd=not detected
Table 7. Total U(VI) desorbed from sediments at various sampling locations from integrations of total desorbed U(VI) curves. U(VI) released relative to Br breakthrough curves is also shown.

<table>
<thead>
<tr>
<th>Well, Depth</th>
<th>Total U(VI) integral (mol-hr/L)</th>
<th>Total U(VI)/Br integral (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LR-17, 6.40 m bgs</td>
<td>1.1E-04</td>
<td>6.5E-07</td>
</tr>
<tr>
<td>LR-17, 7.32 m bgs</td>
<td>1.1E-05</td>
<td>2.1E-07</td>
</tr>
<tr>
<td>LR-17, 7.62 m bgs</td>
<td>1.3E-05</td>
<td>1.7E-07</td>
</tr>
<tr>
<td>LR-21, 6.40 m bgs</td>
<td>5.8E-05</td>
<td>7.9E-07</td>
</tr>
<tr>
<td>LR-21, 7.32 m bgs</td>
<td>1.9E-05</td>
<td>5.1E-07</td>
</tr>
<tr>
<td>LR-21, 7.62 m bgs</td>
<td>2.6E-05</td>
<td>4.5E-07</td>
</tr>
<tr>
<td>LR-25, 6.40 m bgs</td>
<td>2.4E-05</td>
<td>8.3E-07</td>
</tr>
<tr>
<td>LR-25, 7.32 m bgs</td>
<td>2.8E-05</td>
<td>7.4E-07</td>
</tr>
<tr>
<td>LR-25, 7.62 m bgs</td>
<td>3.7E-05</td>
<td>6.9E-07</td>
</tr>
</tbody>
</table>

*Total desorbed U(VI) curves were created by subtracting the predicted U(VI) concentration based purely on mixing of the tracer with native groundwater from the observed U(VI). Integrations were performed for only the positive part of the curve (desorption phase).
Table 8. Transport model input and output parameters for three depths and wells.

<table>
<thead>
<tr>
<th></th>
<th>Well 17</th>
<th>Well 21</th>
<th>Well 25</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6.40 m</td>
<td>7.32 m</td>
<td>7.62 m</td>
</tr>
<tr>
<td></td>
<td>6.40 m</td>
<td>7.32 m</td>
<td>7.62 m</td>
</tr>
<tr>
<td></td>
<td>6.40 m</td>
<td>7.32 m</td>
<td>7.62 m</td>
</tr>
</tbody>
</table>

**Input parameters**

<table>
<thead>
<tr>
<th></th>
<th>Well 17</th>
<th>Well 21</th>
<th>Well 25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Mineral density (kg/L)</td>
<td>2.65</td>
<td>2.65</td>
<td>2.65</td>
</tr>
<tr>
<td>Transport distance (m)</td>
<td>1.36</td>
<td>1.36</td>
<td>1.36</td>
</tr>
<tr>
<td>Injection duration (h)</td>
<td>175.4</td>
<td>52.2</td>
<td>73.0</td>
</tr>
<tr>
<td>Mass fraction &lt; 2 mm</td>
<td>0.60</td>
<td>0.64</td>
<td>0.64</td>
</tr>
<tr>
<td>&lt; 2 mm SA (m²/g)</td>
<td>2.70</td>
<td>2.35</td>
<td>2.35</td>
</tr>
<tr>
<td>Desorbable U(VI) (nmol/g)</td>
<td>0.42</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>Aqueous U(VI) (mM)</td>
<td>0.18</td>
<td>0.17</td>
<td>0.15</td>
</tr>
</tbody>
</table>

**Model-derived parameters**

<table>
<thead>
<tr>
<th></th>
<th>Well 17</th>
<th>Well 21</th>
<th>Well 25</th>
</tr>
</thead>
<tbody>
<tr>
<td>v (m/d)</td>
<td>0.16</td>
<td>1.10</td>
<td>1.01</td>
</tr>
<tr>
<td>D (m²/d)</td>
<td>0.155</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>µ (ln(h⁻¹))</td>
<td>-4.17</td>
<td>-3.23</td>
<td>-3.21</td>
</tr>
</tbody>
</table>

*Parameters estimated from the average of two well cores.*

*Optimized parameters obtained using UCODE. v and D were optimized simultaneously by fitting Br breakthrough curves, while µ was subsequently optimized by fitting the U(VI) curves.*

*D values were fixed in these cases, such that only v was optimized.*
Figure 1. The Old Rifle field site location is shown along with locations of experimental plots and a schematic of Experimental Plot B showing layout of observation wells, including 10.2 cm and multi-level sampling (MLS) wells. Plots A and C are areas used for biostimulation experiments.
Figure 2. Diagram showing construction and completion of multi-level sampling (MLS) wells.

Port 6 was not used. A 7.6 cm channel was cut into the side of each port at the proper depth and covered with 15.2 cm of screen. Plugs are inserted in each port below the zone of intake.
Figure 3. Dissolved U(VI) and Mn concentrations in MLS wells in the study area as a function of depth. Horizontal bars indicate the median values for each depth. Water samples were collected in June 2009 (upper panel) when water levels were close to their peak (3.7-3.8 m bgs) allowing for sampling of some of the 3.7 m bgs sampling ports as well as in September 2008 (lower panel) before the tracer test.
Figure 4. Breakthrough curves for Br, U(VI), and alkalinity at 5.49, 6.40, and 7.32 m bgs in the two injection wells. Br and alkalinity concentrations are normalized with respect to injectate concentrations.
Figure 5. Breakthrough curves for Br, U(VI), and alkalinity at 6.40 and 7.32 m bgs and at 1.36 m, 3.17 m, and 4.74 m downgradient from injection. Br and alkalinity concentrations are normalized with respect to injectate concentrations. Equilibrium model fits of Br and alkalinity data are shown as lines.
Figure 6. Breakthrough curves showing Br and $^2$H concentrations normalized with respect to injectate concentrations 1.36 m downgradient from the injection at 6.40 and 7.32 m bgs.
Figure 7. Breakthrough curves showing dissolved Ca, Mg, and Na concentrations at 6.40 and 7.32 m bgs and at 1.36 m, 3.17 m, and 4.74 m downgradient from injection. Equilibrium model fits are shown as lines.
Figure 8. Breakthrough curves showing pH and calcite saturation index (SI) at 6.40 and 7.32 m bgs and at 1.36 m, 3.17 m, and 4.74 m downgradient from injection. Equilibrium model fits are shown as lines.
Figure 9. Breakthrough curves showing U concentrations (symbols) and equilibrium model fits (lines) for two wells at 1.36 m (LR-17) and 3.17 m (LR-21) downgradient from injection and 6.40 m bgs.
Figure 10. Breakthrough curves showing U concentrations (symbols) and mass transfer (rate-limited) model fits (lines) at 6.40 and 7.32 m bgs and at 1.36 m, 3.17 m, and 4.74 m downgradient from injection. Solid lines show the model fits with optimized $\mu$ and dashed lines are model fits using average $\mu$. 
Figure A1. Model simulations obtained with adjustments in immobile porosity, $\theta_{im}$, and rate constant distribution width, $\sigma$. Results are shown for parameter adjustments to +50% (dotted lines) and -50% (dashed lines) of their original values, both while holding the distribution mean, $\mu$, constant at its originally-optimized value (gray lines) and after reoptimization of $\mu$ (black dotted and dashed lines).
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