

Uranium Reduction in Sediments Under Diffusion-Limited Transport of Organic Carbon

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Introduction

Uranium (U) is an important subsurface contaminant at sites associated with its mining and processing for energy and weapons production. Because of its high solubility under acidic and alkaline conditions, leakage of such extreme pH U solutions can lead to its highly elevated concentrations in contaminated soils and sediments. The high costs of excavating and disposing soils and sediments containing elevated levels of U, as well as other actinides and metals have motivated consideration of less expensive in-place treatment strategies that transform these contaminants into insoluble forms. A general approach under development for in-situ remediation of U-contaminated sediments involves stimulation of indigenous microorganisms to bioreduce mobile U(VI) to insoluble U(IV) by injection of organic carbon (OC) [1]. Effective distribution of OC in the subsurface remains a challenging technical problem. In bioremediation of subsurface contaminants, injection of OC solutions can result in permeability reduction within the delivery zone because of biofilm buildup. Periodic OC injection is one strategy that may minimize such fouling from biofilm growth. In addition, modeling studies indicate that pulsed nutrient injection can result in more effective remediation. Regardless of the method of placement into contaminated groundwater, OC will preferentially move through sparse networks of interconnected higher permeability flow paths, thereby largely bypassing most of the contaminated subsurface. Thus, short-term infusion of reactants into the subsurface is commonly inefficient because of the combination of very small regions associated with high flow networks and much larger volumes in which transport is diffusion-limited [2]. Where does U reduction occur within diffusion-limited domains that make up most of the subsurface? Are U concentrations measured in groundwater samples from monitoring wells reliable indicators of remediation? Are microbial community distributions spatially correlated with U redox status within diffusion-limited systems? This laboratory study was designed to address these questions.

Methods

The field scenario simulated in this laboratory experiment is that of periodic OC solution injection into U(VI)-contaminated sediments. Our focus is on U redox transformations within lower permeability regions where OC is mineralized while it diffuses in from higher permeability channels. The interaction between advectively accessible preferential transport paths and low permeability sediment blocks is represented in the laboratory model by

placement of an OC solution reservoir in hydrostatic contact over one end of a small soil column. The column design and soils used were described in companion studies on U(VI) diffusion [3] and sorption [4]. Solutions containing 3 mM $\text{UO}_2(\text{NO}_3)_2$ were adjusted to either pH 2 or pH 12, with HCl or NaOH. Each solution was then mixed into two different initially air-dry soils; one from Oak Ridge National Laboratory, TN (denoted OR2 and OR12 for pH 2 and pH 12 uranyl solutions, respectively), and the other from Altamont Pass, CA (denoted AL2 and AL12). The solution:soil mass ratio achieved upon packing the wet, well-mixed sediments into columns was 0.45 ± 0.05 , resulting in initial U(VI) concentrations of $323 \pm 36 \mu\text{g (g soil)}^{-1}$ and initial pore water NO_3^- concentrations of 6.2 and 9.0 mM for the OR and AL soils, respectively (the latter soil having a high native NO_3^- concentration). The 12.7 mm diameter, approximately 55 mm deep soil columns were maintained under hydrostatic conditions, with OC solutions of tryptic soy broth periodically applied by pooling at the top surface of the soils. These solutions were prepared at OC concentrations of 6.7 and 67 mM. Each application consisted of 9.0 mL of one of these OC solutions (after removing the previous pool), and amounted to adding 6.3 or 63 $\mu\text{mol OC per g soil}$, for the low and high OC solutions, respectively. OC solutions were replaced 9 times per column over the 20 month experiment, at 2 to 4 month intervals. This rate of solution replacement was equivalent to average supply rates of 0.09 and 0.9 $\mu\text{mol OC (g soil)}^{-1} \text{ day}^{-1}$. In addition to these treatments, one set of soils was maintained as a control, ponded with a NaCl (0.86 mM), K_2HPO_4 (0.14 mM) solution (matching the concentrations of these salts present in the tryptic soy broth solutions containing 6.7 mM OC). Each column was monitored through measurements in its reservoir (pH, U, and OC concentrations) and soil (redox potential, U(VI) and U(IV) concentrations).

Concentration profiles for U(VI) and U(IV) were obtained by micro-XANES spectroscopy [5]. One side of each column wall was milled to a thickness of 1.0 mm to enhance transmission of incident and fluorescent X-rays. A wide incident beam size (about 0.2 mm vertical by 1.0 mm horizontal) was used in order to obtain oxidation states characteristic of many grains, surfaces, and pores at each measurement location. These measurements were obtained on Day 257 at beamline X26A of the National Synchrotron Light Source, and on Days 150, 361, and 600 at the GSECARS microprobe beamline, Advanced Photon Source. The U(VI) fractions in soils were determined by comparing their U L_{III} absorption edge energies at half step height to those of reference compounds [6]. Our reference compounds were UO_2 powder diluted to 1% in silica

powder, and a 4 mM $\text{UO}_2(\text{NO}_3)_2$ aqueous solution. Concentrations of total U were determined from magnitudes of the U L_{III} absorption edge step (before normalization to unit magnitude).

Results

Because all soil columns treated with 6.7 mM OC showed no significant differences in responses relative to the +0 OC treatments, only comparisons between +0 and +67 mM OC will be described here. Reservoir solutions stabilized to pH values that reflected influences of soil properties, the initial U(VI) solution pH, and redox reactions. Buffering by calcium carbonate brought all AL and the initially pH 12 OR reservoir solution pH values to 8.0 ± 0.5 within the first 40 days. The initially pH 2 OR soil remained slightly acidic ($\text{pH } 6.0 \pm 1.0$) without addition of OC, while the corresponding system treated with 67 mM OC had its pH increased to 7.6 ± 0.9 within the first 40 days. This OC-dependent pH increase probably resulted from proton depletion during Fe(III) and Mn(IV) reduction. The redox potential measurements showed continuously oxidizing conditions in soils lacking OC addition, and more reducing conditions in soils receiving OC. It should be kept in mind that the various redox couples are not in equilibrium, and that Pt electrodes are largely responding to the Fe(III)/Fe(II) couple. Decreases in profile-averaged redox potentials were observed shortly after all OC additions. Analyses of OC in reservoirs indicated about 95% depletion within 100 days. The need to periodically replenish OC in order to sustain reducing conditions is reflected in tendency of redox potentials to return to otherwise high levels. Depth profiles of redox potentials reflected diffusion-limited OC transport and consumption. The reduction front reached depths of about 35 to 45 mm with the periodic OC applications. The deepest regions of these columns remained continuously oxidizing throughout the experiment.

Profiles of U oxidation states in the soil columns obtained by μ -XANES spectroscopy were largely consistent with redox measurements. Correlations between measured U oxidation states and measured redox potentials from all columns exposed to 67 mM OC showed that U reduction was largely associated with Pt electrode redox values in the narrow range of -0.20 ± 0.05 V. Soils that were not treated with high OC solutions exhibited insignificant reduction, i.e. U(VI) accounted for at least 93% of the total U. In contrast, soil columns that were periodically exposed to high (67 mM) concentrations of OC experienced U reduction in regions closest to the OC source. Comparisons of that U oxidation state profiles obtained at different times indicate that the U reduction front was advancing relatively rapidly up to some time between days 150 and 257. Thereafter, the U reduction front remained at fairly fixed depths, in the range of 35 to 45 mm. Thus, the periodic OC treatments established stable U redox stratification with reduced U(IV) soils closest to the OC source, overlying the deeper soil region containing unreduced U(VI). Note that information on U redox stratification would be unavailable from any bulk soil analyses that averages over several cm distances.

Discussion

The sustained steep gradients in redox potential and U(VI)/ Σ U at about the 40 mm depth in the soils treated with high concentrations of OC indicates that diffusion of redox-sensitive species continued to occur across this zone up to 600 days. Thus, transport of NO_3^- , Fe^{2+} , and aqueous U(VI) carbonate species is inferred. We had no way to measure NO_3^- in these small soil columns, but the redox electrodes indicate that Fe(III) reduction did not occur beyond ≈ 40 mm depth. Apparently, diffusive/reductive loss of NO_3^- (initially 6 to 9 mM) was too slow in the deeper soils to allow Fe(III) reduction to begin below this depth. Diffusion of Fe^{2+} from the shallower reducing soils to the oxidizing region was qualitatively evident from formation of red-orange precipitates (presumably $\text{Fe}(\text{OH})_3$) in the 35 to 45 mm depths. Diffusion of U(VI) from the deeper region into the overlying reducing zone was clearly observed in the AL soils supplied with 67 mM OC, but not in the OR soils. Higher mobility of U(VI) in the AL soils than in the OR soils was evident from magnitudes of their concentration maxima in the surface soil region, and from differences in their concentrations profiles at greater depths. This is consistent with much weaker U(VI) sorption measured on the AL soils relative to the OR soils in the range of pH 7 to 8 [4], resulting in higher apparent U(VI) diffusivities in the AL soils [3]. Because the AL soil contains a large fraction of CaCO_3 (10%) and the OR soil has very little ($\approx 0.1\%$), and because the very stable aqueous $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ species [7] appears to be responsible for minimizing U(VI) sorption [4], we believe that $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3(\text{aq})$ is responsible for the observed greater U(VI) mobility in the AL soils.

This study shows that, in diffusion-limited regions of the subsurface, reductive U precipitation zones slowly propagate away from the vicinity of OC delivery. Stratification of redox potentials, microbial communities, and U oxidation state can be very distinct and well correlated. Large regions of the subsurface can retain unreduced U(VI) for long times after accessible outer regions have experienced bioreduction to U(IV) under diffusion-limited stratification. This is especially true when NO_3^- or other oxidants are present as a co-contaminant with U. Because groundwater monitoring is strongly biased towards interconnected higher permeability regions, it may largely sample regions where OC is easily delivered and U reduction is practically complete. Monitoring of remediation by such means has low sensitivity to diffusion-limited domains. These under-sampled, hydraulically passive regions can account for most of the subsurface and not only retain most of the U, but retain it over long times as U(VI).

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