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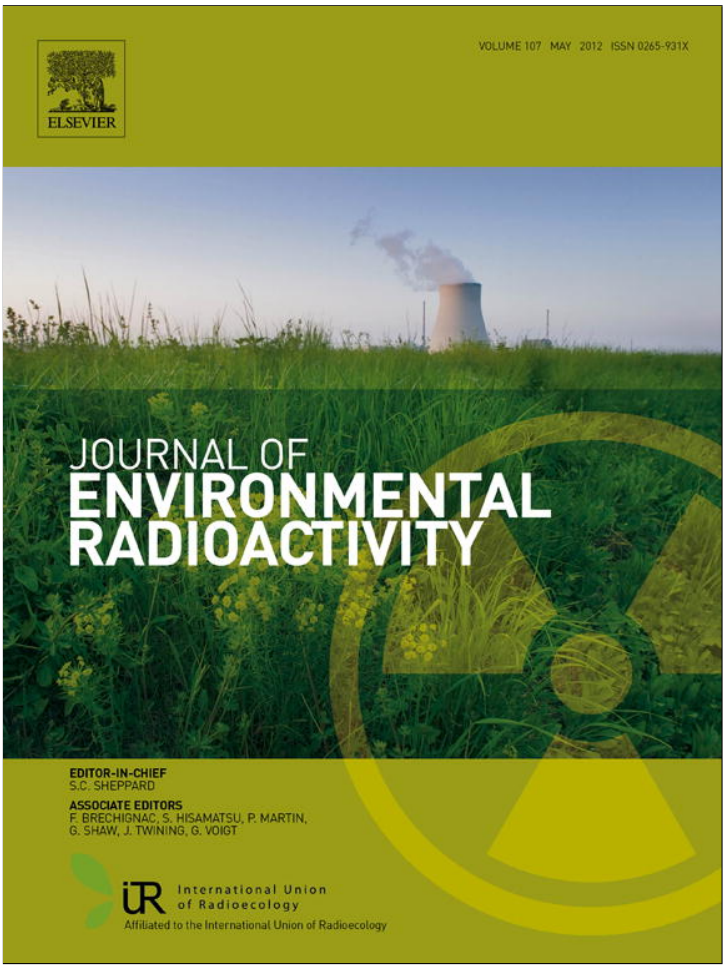

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Short communication

Uranium release from different size fractions of sediments in Hanford 300 area, Washington, USA

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ABSTRACT

Stirred-flow cell tests were carried out to investigate uranium (U) release from different size fractions of sediments from the U.S. Department of Energy's Hanford 300 Area in Washington, USA. Results show that the measured concentration of U release varies with different size fractions, with the fine-grained mass fractions (<75 μm, 75–500 μm, and 500–2000 μm) being the main U carriers. However, because the sediment is mainly composed of gravel (2000–8000 μm) materials, the gravel fraction is a non-negligible U pool. Our elution experiments give a value of 8.7% of the total U being in the gravel fraction, significantly reducing the current uncertainty in evaluating U inventory. A log–log plot of released U concentration vs. elution volume (i.e., elution time) shows a power-law relationship for all size fractions, with identical exponents for the three fine size fractions (−0.875). For the <2000 μm mass fraction, comparing our eluted U values with reported total U concentrations, we estimate that a lower bound value 8.6% of the total uranium is labile. This compares well with the previously published value of 11.8% labile U after extraction with a dilute extractant for three weeks.

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1. Introduction

Uranium (U) is the contaminant of greatest concern at the U.S. Department of Energy's Hanford 300 Area in Richland, Washington (Qafoku et al., 2005). The effect of geochemical conditions on U mobilization has been intensively studied (Dong et al., 2005; Liu et al., 2008, 2009), and some strategies, such as phosphate amendment, have been proposed to control the migrating U plume (Shi et al., 2009).

Sediments in the Hanford 300 Area are up to 92% wt gravel and cobbles (>2 mm) (Arai et al., 2007). However, most research has focused on the fine-grained (<2 mm) sediments, as they are recognized as the main U carrier leading to groundwater contamination. For example, Liu et al. (2008) reported that a significant portion (16–100%) of adsorbed U(VI) was associated with the reactive mass fraction (<2 mm) at the Hanford site; the uncertainty in the figure is due to the paucity of information on U distribution in the coarse (>2 mm) fraction.

To our knowledge, few studies have investigated U concentration in, and release from, different size fractions, particularly the gravel particles, of Hanford 300 Area sediments. This work uses stirred-flow cell experiments to assess the relative contributions of different size fractions with respect to U distribution and release.

2. Materials and methods

2.1. Materials

Sediment samples were collected from the smear zone, at a depth of 3 m below ground surface, beneath the North Process Pond in Hanford 300 Area. Sediment was air-dried and dry-sieved to four size fractions (<75 μm, 75–500 μm, 500–2000 μm, and 2000–8000 μm). We also used a <2000 μm sample, for comparison with other research (Qafoku et al., 2005; Liu et al., 2009; Yin et al., 2011).

Synthetic groundwater (SGW), approximating the composition of groundwater in the Hanford 300 Area (Qafoku et al., 2005), was prepared as the influent solution for the stirred-flow cell tests. The pH of SGW was adjusted to 7.8–7.9.

2.2. Stirred-flow cell test

The U release experiment was performed on each of the five sediment size fractions, using 10-mL stirred-flow cell reactors

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(Millipore, Bedford, MA). The stirred reactor has potential advantages over conventional packed column or batch reactors because it isolates intraparticle rate limitations from advective-dispersive transport, while allowing changes in flux for analysis of sorption kinetics under dynamic conditions (Randle and Hartmann, 1987; Sparks, 1989; Heyse et al., 1997).

The stirred reactor has an influent port at the top, and an effluent port at the bottom. The SGW was spiked with $KReO_4$, giving 120 μg/L ReO_4^- as a non-sorbing tracer to evaluate the retarded release of U. For each size fraction, the SGW was pumped by a HBI Multistaltic pump (Haake Buchler Instruments, Austin, TX) into a stirred reactor containing 0.5 g sediment, resulting in a 50 g/L solid-to-solution ratio based on the cell volume of 10 mL. The outflow rate was maintained at about 0.1 ml/min, as measured by the effluent volume, throughout the 10 day experiment. Sediment was kept suspended in the reactor by a magnetic stirring bar with plastic coating to minimize disintegration of sample particles. The mixed slurry passed through a 0.2 μm pore-size Supor membrane (Pall Corp., Port Washington, NY) placed on the effluent port, then effluent samples were collected in polystyrene tubes by an automatic fraction collector (Spectra/Chrom CF-1, Spectrum Chromatography, Houston, TX). The U concentration in the effluent samples was analyzed using ICP-MS (Perkin–Elmer SCIEX ELAN® DRC II, Sheldon, CT). The pH of selected effluent samples was measured using a small-bore (4.8 mm dia. and 130 mm long) combined pH microelectrode (PHW-17SS, IQ Scientific Instruments, Loveland, CO).

3. Results and discussion

Uranium release experiments for the gravel fraction (2000–8000 μm) were conducted twice, because of the small number of gravel grains (to have about 0.5 g for all size fractions) placed in the reactor. Reproducible results of U release are obtained for the duplicate experiments (Fig. 1), indicating the consistency of the experimental approach. Following a rapid initial release within the first 20 cell volumes (the cumulative effluent volume divided by the 10-ml reactor volume), the effluent U concentration slowly decreased with a long tailing behavior. The measured concentration of the ReO_4^- tracer remained constant over the experimental duration (Fig. 1).

Effluent U concentration from the gravel (2000–8000 μm) fraction was lower than that from other size fractions throughout the elution experiment (Fig. 2). For all size fractions, effluent U

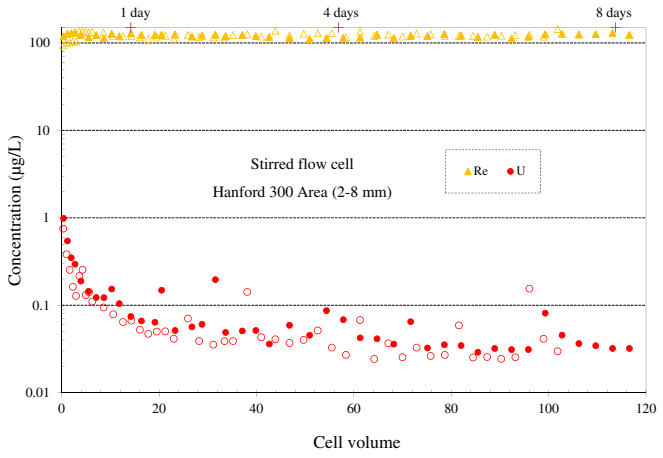

Fig. 1. Measured concentrations of U and ReO_4^- in stirred-flow cell effluent from the 2–8 mm size fraction of Hanford sediment. Filled and empty symbols represent duplicate runs.

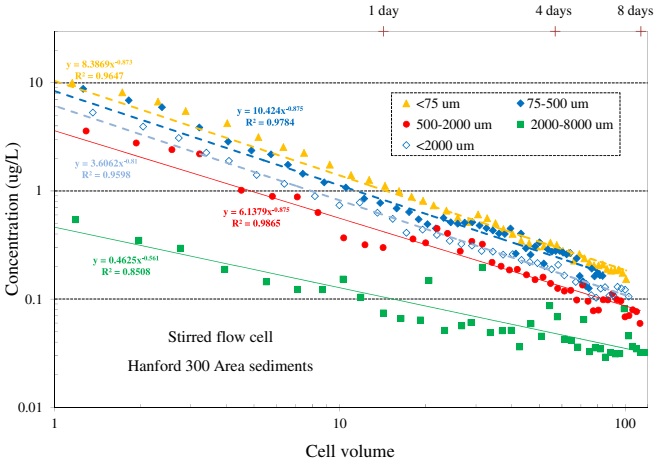

Fig. 2. Comparison of U concentration in stirred-flow cell effluent from different size fractions of Hanford sediment.

concentrations after elution of 100+ cell volumes are still higher than the measured background U concentration of 0.02 μg/L (0.084 nmol/L) for the influent SGW. This long tailing is probably due to rate-limited mass transfer processes, such as kinetic desorption from the fine fraction, and diffusive transport within intragranular pores for the gravel fraction. No appreciable change was observed in the effluent pH; with measured influent pH of 7.78, the effluent pH values for all size fractions were 7.65 ± 0.033.

A log–log plot of released U concentration vs. elution volume (i.e., elution time) exhibits a power-law relationship for all size fractions (Fig. 2). Notably, exponents for the three fine size fractions are essentially identical (−0.875), while the exponent for the gravel (2000–8000 μm) fraction is −0.561; the lower exponent indicates a slower release rate. The different exponents may indicate different mass transfer processes (chemically- and/or physically-limited release). Release of U is probably controlled by chemically-related desorption in three fine size fractions, compared to physically-based diffusion and chemical desorption in gravel fraction. Mechanistic understanding using grain-scale diffusion or mass transfer models (e.g., Liu et al., 2009) to simulate the release data will be pursued to further clarify the underlying process(es) for U release in different size fractions.

We are not aware of other reports of power-law release behavior for stirred-flow cell experiments. However, Hadermann and Heer (1996) and Haggerty et al. (2000) reported that rate-limited mass transfer processes caused the breakthrough curve in column experiments to behave as a power-law at late time, with an exponent of −1.5 indicating a diffusion-limited mass transfer process. Using the fitted power-law relationships for the different size fractions, we see that large elution volumes are needed to reach U background. For example, 1009 cell volumes would be needed for the <75 μm fraction effluent to reach the background U concentration of 0.02 μg/L (Table 1).

The cumulatively released U for each size fraction, at the end of stirred-flow cell tests with similar duration and eluted volume, shows that both the <75 μm and 75–500 μm fractions released more than 10 times as much U as the gravel fraction (Table 1). However, considering that the gravel fraction makes up 42% by mass of the 300 Area sediment studied in this work, we find that the gravel fraction contains 8.7%–9.3% (Table 1) of the labile U. Liu et al. (2008) reported that the <2000 μm fraction may contain from 16% to 100% of the total U; by difference, the gravel and cobbles (>8 mm) combined may contain from 0% to 84% of the U. This wide range of uncertainty comes from the difficulty in quantifying U in

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Table 1
Distribution of U as a function of size fractions of Hanford sediment.

Size fraction (μm)	Mass fraction (%)	Labile U (μg/g)	Labile U fraction (%)	Expected cell volume for complete U release
<75	4.42	1.90	12.4	1009
75–500	20.3	1.49	44.9	1274
500–2000	33.4	0.69	34.0	695
2000–8000	41.8	0.14	8.7	270
<2000	58.2	0.98	90.7[a]	610

[a] Using the <2000 μm fraction, labile U in the 2000–8000 μm fraction is 9.3% of total labile U.

coarse particles, and the relatively few studies focusing on the coarse fraction. The present work significantly constrains the assessment of U distribution across particle size fractions. Furthermore, the measured released U of 0.98 μg/g for <2000 μm materials is very comparable to 1.06 μg/g calculated from the weighed mass fraction and measured U content for <75 μm, 75–500 μm, and 500–2000 μm size fractions; this further indicates the data quality of the experimental approach.

Comparing our elution estimates with Liu et al.'s (2008) U(VI) concentrations, we can also estimate the fraction of U that is labile. Based on the reported total U(VI) concentration of 57.8 nmol/g (11.4 μg/g) by Liu et al. (2008), and 0.98 μg/g released U from the stirred-flow cell, only 8.6% of the sorbed U(VI) in the <2000 μm fraction is labile. This is a lower bound, because we did not leach to equilibrium (Fig. 2). For comparison, Qafoku et al. (2005) found <22.7 μmol/kg total U by X-ray fluorescence, and the "indigenous" U(VI) labile fraction, mobilized after 3 weeks of treatment with a pH 9.45 solution of 1.44×10^{-2} mol/L $NaHCO_3$ and 2.8×10^{-2} mol/L Na_2CO_3, was 2.68 μmol/kg or 11.8% of the total.

4. Conclusions

This study examines different size fractions of Hanford 300 Area sediments, with respect to the distribution and release of contaminant U. The gravel (2000–8000 μm) fraction contains 8.7%–9.3% of the smear zone sediment's labile U. We also find that approximately 8.6% of the U in the fine (<2000 μm) fraction can be considered labile, that is, relatively susceptible to release into the groundwater. We conclude that U releases from Hanford 300 area sediment via mass transfer limited processes poses a long-term threat of groundwater contamination.

Acknowledgements

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