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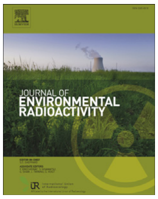

Retention and chemical speciation of uranium in an oxidized wetland sediment from the Savannah River Site

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ABSTRACT

Uranium speciation and retention mechanisms onto Savannah River Site (SRS) wetland sediments was studied using batch (ad)sorption experiments, sequential extraction, U L_3-edge X-ray absorption near-edge structure (XANES) spectroscopy, fluorescence mapping and μ-XANES. Under oxidized conditions, U was highly retained by the SRS wetland sediments. In contrast to other similar but much lower natural organic matter (NOM) sediments, significant sorption of U onto the SRS sediments was observed at $pH < 4$ and $pH > 8$. Sequential extraction indicated that the U species were primarily associated with the acid soluble fraction (weak acetic acid extractable) and organic fraction (Na-pyrophosphate extractable). Uranium L_3-edge XANES spectra of the U-bound sediments were nearly identical to that of uranyl acetate. Based on fluorescence mapping, U and Fe distributions in the sediment were poorly correlated, U was distributed throughout the sample and did not appear as isolated U mineral phases. The primary oxidation state of U in these oxidized sediments was U(VI), and there was little evidence that the high sorptive capacity of the sediments could be ascribed to abiotic or biotic reduction to the less soluble U(IV) species or to secondary mineral formation. Collectively, this study suggests that U may be strongly bound to wetland sediments, not only under reducing conditions by reductive precipitation, but also under oxidizing conditions through NOM-uranium bonding.

1. Introduction

Uranium (U) accumulates in wetlands in areas where U-rich rock formations are present (Zielinski et al., 1987). Natural and constructed wetlands have been used as a cost-effective means to immobilize U from U mines and processing facilities (Noller et al., 1994). Thus, understanding the biogeochemical processes of U in the wetlands is important for predicting risk associated with U contamination (e.g., U mine and milling sites, nuclear waste storage sites, and fuel cell rod storage basins). Possible pathways for long term U immobilization in wetlands include the chemical and/or microbial reduction of soluble U(VI) ions to fairly insoluble U(IV) species (Kalin et al., 2005; Lovley et al., 1991; Noubactep et al., 2006; Turick et al., 2008), mineral precipitation, sorption onto NOM (Wan et al., 2011), ion exchange or sorption to sediment minerals (Akber et al., 1992; Dong et al., 2012; Grybos et al., 2007), accumulation in plants (Hinton et al., 2005; Knox et al., 2008), and incorporation into secondary minerals (Lind et al., 2013a).

The Savannah River Site (SRS) in Aiken, SC includes several (former) uranium processing facilities. As a result of their operations, U has entered the surrounding environments through accidental and purposeful discharges. For example, approximately 45,000 kg of depleted U was released into Tims Branch and its associated wetlands between 1958 and 1980 and approximately

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70% of the U still remains in the stream and associated wetland sediments of this waterway (Bertsch et al., 1994; Evans et al., 1992; Pickett, 1990).

The U desorption distribution coefficients (K_d values) of SRS contaminated wetland sediments has been measured to be quite large, ranging from 170 to 6493 mL/g (Kaplan and Serkiz, 2001). NOM has been demonstrated to control the availability of U in the contaminated sediments within Tims Branch (Sowder et al., 2003). Bertsch et al. (1994) reported the *in situ* characterization of chemical speciation of U in the sand fraction of a SRS sediment sample using micro X-ray absorption spectroscopy, which appeared to indicate the presence of U(VI). Given these initial observations, the remediation technologies of the contaminated SRS sediments with apatite ($Ca_{10}(PO_4)_6(OH, F)_2$) (Arey et al., 1999; Kaplan and Knox, 2004; Seaman et al., 2001), humic acid (Wan et al., 2011), native trees (Hinton et al., 2005), natural hyper-accumulators (e.g., the netted chain fern (*Woodwardia areolata*)) (Knox et al., 2008), and microbial metabolites (Turick et al., 2008) have been evaluated.

However, the chemical speciation of U and the molecular mechanisms responsible for its high retention in the SRS wetland sediments reported by Kaplan and Serkiz (2001) are not sufficiently well understood. What remains unclear is the strong U retention mechanism, even under oxidizing conditions where U(VI) oxidation state is expected to predominate. The tendency of U to enter the mobile phase and become available to local biota or be transported from the contaminated area has not been well quantified. Additional information is also needed to facilitate the development of *in situ* treatment and remediation strategies of U-contaminated SRS wetland sediments. The objective of this work was to identify (1) the chemical speciation of U; and (2) the possible molecular mechanisms responsible for the high U retention in SRS wetland sediments under oxidizing conditions.

2. Materials and methods

The general approach was to conduct laboratory batch tests to measure U sorption as a function of pH with SRS uncontaminated wetland sediments, and then to use sequential extraction, U L_3-edge XANES spectroscopy, fluorescence mapping and μ-XANES to evaluate the U speciation of spiked laboratory samples and U-contaminated wetland sediments.

2.1. Artificial groundwater

The recipe for an artificial groundwater (AGW) solution was based on the monitoring survey results for uncontaminated groundwater samples at the SRS (Strom and Kaback, 1992). Briefly, the AGW has a pH of ~6.0, electrical conductivity of 0.026 mS/cm, turbidity of <1 NTU (Nephelometric Turbidity Units), 1.25 mg/L Na, 0.25 mg/L K. 0.93 mg/L Ca, 0.66 mg/L Mg, 5.51 mg/L Cl, and 0.73 mg/L SO_4, which mimics the non-impacted SRS subsurface groundwater conditions (Li et al., 2012).

2.2. SRS wetland sediments

Contaminated and uncontaminated surface sediment samples (0–0.15 m depth below the leaf-litter level) were collected from the wetland site, which is adjacent to a pilot-scale nuclear facility that released processing wastes including U and Th into an unlined seepage basin between 1958 and 1980. The basin contents entered the adjacent wetland by subsurface flow and overland flow. The characteristics of the contaminated and uncontaminated sediments are summarized in Table 1 (Kaplan and Serkiz, 2001). The mineralogy of both the contaminated and uncontaminated sediments was characterized by primary silica sand, lesser kaolinite, hydroxy-interlayered vermiculite, illite and gibbsite, and little Fe oxides.

Table 1
Characteristics of the SRS contaminated and uncontaminated sediments.

	Contaminated sediment	Uncontaminated sediment
pH[a]	4.53	4.16
Organic carbon, mg/kg	1427	1395
Fe oxide,[b] wt%	0.09	0.01
Sand, wt%	53	79
Silt, wt%	22	16
Clay, wt%	19	6
^{238}U, mg/kg	285	0.57
^{238}U desorption K_d, mL/g	1297	n/a

n/a = not available.

[a] 1:1 solid/deionized water ratio.

[b] Analyzed using Na dithionite-sodium citrate-citric acid extraction, reported as Fe_2O_3.

2.3. Batch experiments

Batch U(VI) sorption experiments as a function of pH (2.5–10) were set up at a constant total U(VI) concentration (2×10^{-5} M) in AGW solution with or without 0.1 M $NaNO_3$ under ambient atmospheric CO_2 ($P_{CO2} = 10^{-3.5}$ atm) and temperature (22 °C). For each set of experiments, a solid-free control was included in doublet. The purpose of these controls was to determine the initial U concentration for K_d calculation (described below) and to provide an indication if any U sorption to the tube walls occurred during the experiment. About 0.1 g of the uncontaminated sediment and 10 mL solution were added into a 15 mL polypropylene centrifuge tube while exposed to air. The resulting solid concentration was 10 g/L. Uranyl nitrate (^{238}U, Electron Microscopy Sciences, Hatfield, PA) was used to make the U stock solution (2×10^{-3} M, pH 3.6, Eh 433 mV). After spiking 0.1 mL of the U stock solution and then pH adjustment using 0.1 M NaOH or 0.1 M HNO_3 solution, the suspensions were placed on a shaker for 96 h sorption reaction. For some batch experiments, all tubes were open to atmospheric CO_2 twice per day and 30 min each time to promote equilibration with atmospheric CO_2. The pH values were adjusted daily until the pH shifts were <0.1 pH unit (a Radiometer Copenhagen PHM 95 pH meter). Each suspension was filtered using 0.2 μm nylon membrane syringe filters. The filtrate was acidified with 2% HNO_3 and analyzed for U by inductively coupled plasma mass spectrometry (ICP-MS) according to EPA Method 200.8, Rev. 5.4 (USEPA, 1994). The ICP-MS analyses had an uncertainty of ±10%, but our repeatability test indicated that this uncertainty was often within ±5%. The extent of U sorption to the sediments was calculated using a distribution coefficient, K_d value, which is a U concentration ratio of sediment to solution. The K_d values (mL/g) were calculated using Equation (1):

$$K_d = \frac{C_0 - C}{C} \times \frac{V}{M} \tag{1}$$

where C_0 is the initial U concentration in the control samples and C is the final U concentration in solutions, V is the volume of the solution (mL) and M is the mass of the sediment (g).

2.4. Sequential extraction

Sequential extraction of contaminated and U-sorbed uncontaminated sediments was carried out using the method of Miller et al. (1986), which was slightly modified in American Society for Testing and Materials (ASTM) D3974-81 (ASTM, 1999) and other literature protocols (Baston et al., 1996; Kaplan and Serkiz, 2001;