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Factors influencing uranium reduction and solubility in evaporation pond sediments[†]

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Abstract. Evaporation ponds in the San Joaquin Valley (SJV), CA, USA that are used for the disposal of irrigation drainage waters, contain elevated levels of U that may be a threat to pond wildlife. The ponds support euryhaline algae, which become incorporated in the sediments as depositional organic matter (OM) – facilitating reducing conditions. Our earlier studies have shown that U in one SJV sediment was primarily present as the highly soluble U(VI) species (as opposed to the less soluble U(IV) species), despite the presence of volatile sulfides. In this research, we investigated the effects of native pond algae (*Chlorella*) and potential reducing agents on U redox chemistry of SJV pond sediments. San Joaquin Valley pond sediments were equilibrated with natural and synthetic pond inlet waters containing approximately 10 mg U(VI) L^{-1} to which reducing agents (acetate, sucrose, and alfalfa shoot) were added. The equilibrations were done under oxic (*Chlorella* only) and O_2-limiting conditions (remaining treatments). Sediments were examined for changes in average U oxidation state by X-ray near-edge absorption structure (XANES) spectroscopy and U concentration by ICP-MS.

For the alfalfa treatments, a 95 percent loss of U(VI) from solution, the presence of sulfides, and results from the XANES studies suggest U(VI) was reduced to U(IV). Upon exposure to air, the precipitated U was readily oxidized, suggesting the reduced U is susceptible to oxidation. Much less reduction of U(VI) was observed in the other 3 treatments and the solid phase was dominated by U(VI) as in the natural pond sediments. A second study was conducted with pond sediment-water suspensions to determine the effects of controlled PCO_2 and low redox potential (Eh) on U solubility. These suspensions were equilibrated at 0.22 and 5.26 kPa PCO_2 and allowed to "free-drift" from an oxidized to a reduced state. At high Eh and high PCO_2, dissolved U concentrations were higher than in the low PCO_2

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systems due to greater complexation with CO_3. Dissolved U concentrations decreased only under intense sulfate reducing conditions, even at low Eh conditions. It appears that U reduction occurred by chemical reduction via sulfide ion. Comparing the XANES data of the pond sediments with the laboratory-produced solids we conclude that biosorption by algae and bacteria is the dominant mechanism depositing U in the sediments. Even though there are organisms that can use U(VI) as a terminal electron acceptor, we found that sulfate reduction was preferred in these high-SO_4 waters. Mixed oxidation state U-solids were preferentially formed in the pond sediments and in the lab except under intense SO_4 reducing conditions.

Abbreviations: SJV – San Joaquin Valley; SR – Sulfate Reduction; TLB – Tulare Lake Bed; XANES – X-ray near-edge absorption structure

Introduction

In the San Joaquin Valley (SJV) of California, elevated levels of uranium (U) are accumulating in evaporation ponds, which receive agricultural drainage waters (Chilcott et al. 1990a,b). These saline, high carbonate-alkalinity ponds often undergo wetting and drying cycles, which can influence the aqueous and solid phase redox chemistry of U. Although avian toxicities have been associated with elevated levels of Se in the ponds and the former Kesterson Reservoir (Merced County, CA) (Ohlendorf et al. 1986), studies have shown that U may have detrimental effects on the pond waterfowl in the SJV (Ohlendorf et al. 1993). In the SJV, over 18,000 acres (7,300 ha) of evaporation ponds exist and most of these ponds have U concentrations which exceed the USEPA recommended drinking water standard of 20 μg U L^{-1} (Chilcott et al. 1990b). In southeastern Colorado, U is also accumulating in drainage waters (Zielinski et al. 1997).

In nature, U has three oxidation states: U(IV), U(V) and U(VI). The highly soluble U(VI) ion always exists as the ion group UO_2^{2+} (uranyl). Uranium(V), which exists as the UO_2^{+} species, is unstable due to disproportionation and is not expected to dominate redox speciation in natural waters. The U(IV) species, which is found as the U^{4+} ion, is sparingly soluble in aqueous systems. Uranium(IV), (V) and (VI) undergo hydrolysis and form soluble complexes with the carbonate ion (CO_3^{2-}) (cited in Grenthe et al. 1992). The U(VI)-carbonate complexes such as $(UO_2)_2CO_3(OH)_3^{-}$, $UO_2CO_3^{o}$, $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$ are the most stable and soluble in oxic environments. These species can be expected to dominate in oxic waters with elevated carbonate alkalinities.

The adsorption of dissolved U(VI) on soil surfaces, clays, carbonate minerals, and metal oxides has been studied (Duff & Amrhein 1996; Waite et al. 1994; Chisholm-Brause et al. 1994; Voudrias & Means 1993; Hsi & Langmuir 1985; Tripathi 1983). Many of these studies conclude that complexation of U(VI) by dissolved CO_3^{2-} results in decreased sorption to natural surfaces (Duff & Amrhein 1996; Hsi & Langmuir 1985; Tripathi 1983). In waters with alkalinities greater than 2 $\text{mmol}_c\ L^{-1}$ HCO_3^- and saturated with calcite ($CaCO_{3(s)}$), U(VI) adsorption on a calcareous SJV agricultural soil was low regardless of PCO_2 (Duff & Amrhein 1996). This low adsorption of U(VI) was attributed to the predominance of the U(VI)-mono-, di-, and tri-carbonate species in solution.

It is generally thought that the reduction of U(VI) to U(IV) results in the formation of the sparingly soluble U(IV) solid $UO_{2(s)}$ (uraninite) in low O_2 environments. This occurs in the development of ore deposits (Spirakis 1996; Osmund & Cowart 1982) and oceanic sediments (Shaw et al. 1994; Anderson et al. 1989). A biologically-mediated reaction with organic matter (OM) and elevated dissolved CO_3^{2-} can be written to describe this reduction (van der Weijden et al. 1990):

$$2UO_2(CO_3)_3^{4-} + CH_2O + 2H^+ + H_2O \longleftrightarrow 2UO_{2(s)} + 6HCO_3^- + CO_{2(g)}$$

Pure cultures of SO_4^{2-} and dissimilatory Fe-reducing bacteria can enzymatically reduce U(VI) to U(IV) (Lovley & Phillips 1992; Lovley et al. 1991). It has been proposed that sulfides can directly reduce U(VI) by the following reaction (Klinkhammer & Palmer 1991; Barnes & Cochran 1993; Langmuir 1978):

$$4UO_2(CO_3)_3^{4-} + 15H^+ + HS^- \longleftrightarrow 4UO_{2(s)} + SO_4^{2-} + 12CO_{2(g)} + 8H_2O$$

These reports all suggest that under anaerobic conditions, sediment U should be dominated by the +IV oxidation state. However, Duff et al. (1997a) reported that U X-ray absorption near-edge structure spectroscopy (XANES) data from highly reducing, sulfidic SJV sediments showed that sediment U was approximately 25% U(IV) and 75% U(VI), a ratio which corresponds closely to that of pitchblende ($U_3O_{8(s)}$). Thus, a more likely reaction to describe the reductive precipitation of U would be:

$$12UO_2(CO_3)_3^{4-} + 47H^+ + HS^- \longleftrightarrow 4U_3O_{8(s)} + SO_4^{2-} + 36CO_{2(g)} + 24H_2O$$

When the anaerobic SJV pond sediments were exposed to air, this mixed oxidation state solid was highly soluble (Duff et al. 1997a). It was concluded that changes in the sediment structure by mechanically stirring the pond surface sediments or the drying of the ponds could result in resolubilization of precipitated U. The potential for releasing U from the sediments is a concern to pond managers should the sediments become disturbed during such processes as dredging and the reworking of pond banks.

Pond algae may influence U redox chemistry. Most ponds in the SJV contain algae that are known to sorb U and ultimately end up as sediment U (Duff et al. 1997a,b). The reduction of Se(VI) by *Chlorella* (a green alga isolated from SJV Pond 14) has been observed in pond water (Fan et al. 1997). This may also be a mechanism by which U(VI) can be taken from the water column and transferred to the sediments as U(IV).

Other potential reductants of sediment U(VI) are acetate and sucrose. They are readily oxidizable carbon sources that become degraded by reductive microbial processes in organic soils (Tate 1979). These simple compounds are easier to degrade than recalcitrant aromatic C compounds such as salicylate (Tate 1979) and they may be oxidized during microbial reduction of U(VI) to U(IV). Alfalfa shoot is a slightly more complex microbial energy C source than acetate and glucose (a constituent of sucrose) due to its more heterogeneous organic matter content. However, it is a good N source. Alfalfa and other similar materials (rice straw) have promoted reducing conditions during studies on elemental cycling and redox chemistry with soil- and sediment-water equilibrations (Duff et al. 1997a; Amrhein et al. 1993; Masscheleyn et al. 1990, 1991).

To examine the oxidation states of U in soils and sediments, highly sensitive techniques such as X-ray absorption near-edge structure spectroscopy (XANES) have been successfully applied *in situ* (Duff et al. 1997a; Morris et al. 1996; Bertsch et al. 1994). The energy of an X-ray absorption edge increases with increasing valence, resulting from the reduced shielding of the nuclear core electrons. This increase in the binding energy of the core levels is often evident by shifts in pre-edge and bound-state edge features in an XANES spectrum and can be correlated to differences in the oxidation state of the cationic center. These XANES studies determined that some U(IV) species are stable with U(VI) species in oxidized soils and sediments (Duff et al. 1997a; Morris et al. 1996; Bertsch et al. 1994).

In this study we investigated the conditions under which U might be reduced to the +IV oxidation state. We used several reducing agents to induce biotic and abiotic U reduction. We measured the oxidation state of U by applying *in situ* XANES techniques, in pond algae grown in synthetic drainage water containing U(VI) and pond sediments equilibrated with U(VI)-containing natural and synthetic pond inlet waters. Additionally, sediment-water suspensions were used to study the effects of dissolved CO_3^{2-} and Eh on U solubility and oxidation state under controlled PCO_2 and variable Eh conditions.

Methods

Description of the San Joaquin Valley, the Kesterson Reservoir, and Pond 14

The SJV consists of over 3 million acres of valley floor in the southern part of the Central Valley of California. It is bound by the Coastal Ranges to the west and by the Sierra Nevada to the east. Most of the irrigation water for the SJV region comes from the Sierra Nevada via the California Aqueduct. Long term crop irrigation and insufficient deep drainage in the SJV area, has resulted in a water table rise from several tens of m to about 1.5 m below the surface at the topographic low in the Tulare Lake Basin (TLB). High temperatures associated with the hot arid climate of Central Valley region promote the evaporation of the shallow ground water at the soil surface and the accumulation of salts in the subsurface. These salts adversely affect crop productivity and water infiltration rates. To contend with rising water tables, subsurface drainage systems are often installed to decrease soil salinity and remove water not used by crops. Prior to 1985, most drainage waters were sent to the Kesterson Reservoir (once part of the Kesterson National Wildlife Refuge, Merced County, CA).

The Kesterson Reservoir located in the northern portion of the SJV, received waters from the SJV via a drainage canal (the former San Luis Drain). The reservoir consisted of 12 shallow basins *or cells* and incoming drainage waters were used for marsh management. After several decades of use, the reservoir was closed after numerous avian abnormalities and mortalities were attributed to elevated levels of toxic trace metals (mainly Se) in the waters and sediments (Ohlendorf et al. 1986).

The SJV ponds (such as Pond 14, as identified in Chilcott et al. 1990a,b) were created after closure of the Kesterson Reservoir in 1985. Evaporation ponds vary in size from about 10 to 2000 acres (4 to 800 hectares) and collectively, they occupy over 9 times the acreage of the former Kesterson Reservoir. Trace element concentrations in the ponds differ with location in the valley. For example, ponds in TLB region tend to have greater concentrations of U relative to other SJV ponds (Chilcott et al. 1990a,b).

Pond 14 is located in the TLB in the western SJV. It is 30 acres (12.1 hectares) in size and periodically receives drainage waters from irrigated fields nearby. When filled, Pond 14 supports a 1-m water column and it is allowed to evaporate to dryness intermittently. Soil near Pond 14 is a fine, montmorillonitic (calcareous), thermic Vertic Fluvaquent. As with most soils in the SJV area, this soil is derived from marine cretaceous shale materials that are high in trace elements, such as V, Se, As, B, Mo and U. As the irrigation waters pass through the soil, the U is leached and when the drainage waters are evaporated, U accumulates in the ponds.

Pond 14 sediments have several surface (0–5 cm) depositional layers of organic material that are easily recognized (described below). These layers formed after numerous wetting and drying cycles, which occur periodically. Relative to deeper sediments, these surface sediments contain elevated levels of U (Duff et al. 1997b). Similar depositional layers in evaporation pond surface sediments have been reported (Chilcott et al. 1990a). Pond 14 was freely accessible for sampling, unlike the majority of ponds in the TLB region. Additionally, the California Aqueduct is the primary source of irrigation water for the cropland associated with Pond 14, making Pond 14 representative of most ponds in the region for this study.

Experiment 1 – Pond 14 sediments equilibrations with inlet waters and reducing agents

Sediment and pond inlet water collection and synthetic water preparation
Surface sediments (0 to 5 cm) consisting of highly stratified layers of depositional material were sampled from the edge of Pond 14, which was nearly full at this time in the summer of 1991. The surface sediment layers were highly visible, very compact and almost saturated with pond water. From the edge of the pond, the surface sediments were easily sampled with hand and shovel and placed in a plastic container as slightly disturbed depositional layers. The sediments were stored at 4 °C under O_2-limiting conditions (tightly covered) under Pond 14 water until use. Approximately 50 g of sediment was removed and gently mixed with a plastic spatula until the remains of the surface layers were no longer evident. No attempt was made to prevent oxidation of the reduced sediment during the brief mixing process. This freshly mixed sediment was added to the waters as described below.

Inlet water from Pond 14 was collected in 1993 from the inlet pipe on the southwestern corner of the pond. The water was collected in well-rinsed, 1.5-L plastic containers, which were filled with minimal headspace, and refrigerated at 4 °C until use. Water was not filtered and the suspended solids were allowed to settle during refrigeration. The upper 0.5 L portion of the inlet water was decanted from the containers and mixed with U(VI) from a stock solution of $UO_2(NO_3)_2$ to give concentrations of 10 mg U(VI) L^{-1}. Major cations were determined by inductively-coupled plasma mass spectrometry (ICP-MS) and major anions were determined by ion exchange (Ion Chromatography, Dionex, Sunnyvale, CA). Carbonate alkalinity was measured by titration with dilute H_2SO_4.

The synthetic pond water was made to have a similar composition to that of the inlet water (Table 1). It was made with deionized water, reagent grade salts so that the major ions were $Na^+$and Cl^- (in meq L^{-1}) and it had a pH of 8.0. Additionally, the waters contained excess reagent grade $CaCO_{3(s)}$ (cal-

Table 1. Experiment 1. The water chemistry was dominated by $Na^+$and Cl^-. PCO_2 for the natural water was calculated to be 0.03 atm (or about 3.03 kPa), a level ten-fold greater than that for pure water in equilibrium with atmospheric CO_2. The synthetic water had a lower carbonate alkalinity and ionic strength than the natural water. The Eh of the synthetic pond water was not measured.

	pH	Eh	EC	Ca^{2+}	Mg^{2+}	Na^+	$SO_4{}^{2-}$	Cl^-	$HCO_3{}^-$
		mV	dS m^{-1}			mmol L^{-1}			$mmol_c$ L^{-1}
Natural Pond 14 Water	7.9	+335	36	11	32	575	120	375	56
Synthetic Pond Water	8.3	—	10	9	4	94	31	75	2

cite, 1 g L^{-1}) and $CaSO_4{\cdot}2H_2O$ (gypsum, 3 g L^{-1}). These salts were added in excess because chemical analyses of the Pond 14 inlet water (described above) indicated the waters were supersaturated with respect to calcite and gypsum (as determined with equilibrium-based thermodynamic calculations, described below). Uranium(VI) from the stock solution was added to the pond waters, to give a concentration of 12 mg U(VI) L^{-1}. The synthetic water was allowed to equilibrate in the presence of atmospheric CO_2 for 48 hours prior to use. The waters were not filtered. Major cations, anions and carbonate alkalinity values were determined as above.

Preparation of waters with reducing agents for sediment-water equilibrations

A culture medium for algae was prepared which contained nutrients, trace metals and vitamins (SMEWW 1992). One-half mL of dilute culture medium and 0.2 mL of a pure *Chlorella* suspension were added to the natural and synthetic waters to give a final volume of 30 mL each. This alga was isolated from Pond 14 and characterized (Fan et al. 1997). The mixtures were prepared in duplicate, shaken, covered loosely to allow the entrance of air, and equilibrated for three weeks at 25 °C in incandescent lighting (16/8 hr light/dark). In duplicate, the U(VI)-containing synthetic and natural pond waters were amended with one of the following treatments: 5.0 g sodium acetate L^{-1}, 5.0 g sucrose L^{-1}, or 1.7 mg ground dried alfalfa L^{-1}. The amended pond waters (30 mL) were equilibrated with 0.1 g of moist Pond 14 sediment in a N_2 headspace in 50 mL polycarbonate centrifuge tubes. The samples were tightly sealed and covered with Parafilm®, shaken gently by hand for one minute per week, and allowed to equilibrate for 3 weeks. The equilibrations were done in the dark to limit the growth of photosynthetic organisms. To account for sorption of U by the centrifuge tubes, the natural and synthetic waters were equilibrated in the absence of sediment or reducing agents. After the

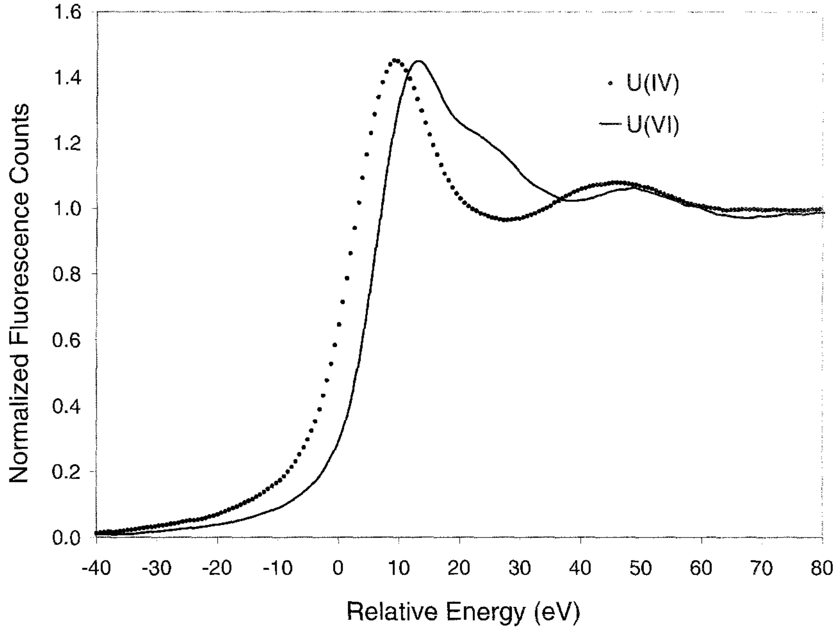

Figure 1. The relative UL_{III} absorption edge position for the U(IV) and the U(VI) solid standards. Increases in the relative energy of the edge position are indicative of increasing average U oxidation state.

3-week incubation period, the amended water mixtures were centrifuged at 17,300 r.c.f. The pH of the supernatants was measured, decanted, and filtered through a 0.45 μm filter. Dissolved U was determined using a Kinetic Phospholuminescence Analyzer (KPA) (Chemcheck Instruments, Seattle, WA, USA). Care was taken to prevent sample quenching from dissolved OM and Cl^- by diluting the samples appropriately and the amount of container adsorption of U was negligible. The centrifuge tube headspaces were purged with N_2 and sediment pellets were prepared for XANES spectroscopy as below.

XANES measurements

The sediment pellets were analyzed for U oxidation state in the solid phase directly using the X-ray microprobe beamline X26A at the National Synchrotron Light Source (Brookhaven National Lab., Upton, NY, USA, Duff et al. 1997a). The sediment pellets were prepared for XANES analyses in an N_2-purged glove box 2 days after centrifugation. A Si(Li) energy dispersive detector having an area of 30 mm^2, was mounted at 90 degrees with respect to the beam. The detector was positioned 2 cm from the sample and used to monitor and collect UL_{III} fluorescence X-rays. A 300 μm by 300 μm beam

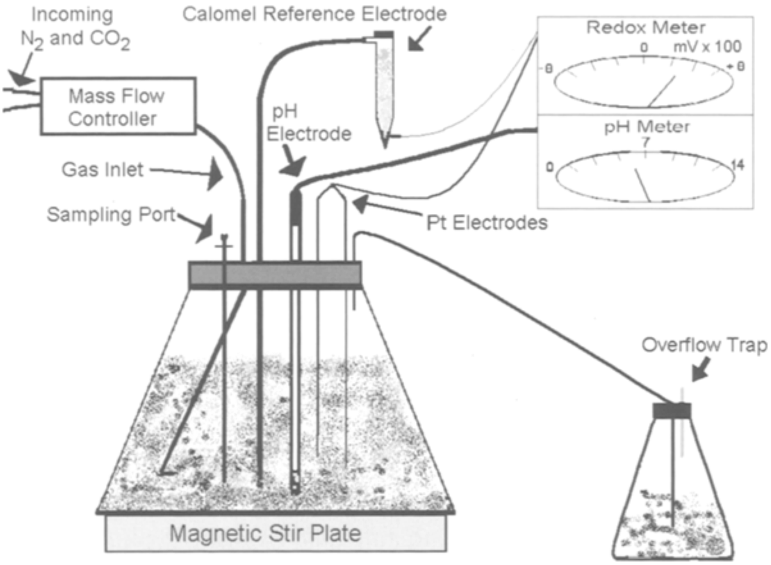

Figure 2. Apparatus for monitoring and controlling PCO_2 and Eh in the sediment-water suspensions, Expt. 2.

was used and the collection time was determined with a monochromator that was tuned 10 eV above the UL_{III} absorption edge and the count rate was observed with the Si(Li) detector. A count rate of 50 cps for the UL_{III} edge was determined and used to calculate the count time per scan point, which gave a scan maximum of >6,000 counts. Eighty seconds per scan point were found to provide adequate counts for the 300 μm X-ray beam size. The XANES spectra were acquired at 0.3 eV step intervals over a 130 eV range, which was relative to 17166 eV. Scan limits were 40 eV less than and 90 eV greater than the UL_{III} absorption edge. Standards consisted of $U(IV)O_{2(s)}$ and U(VI)-acetate (Figure 1). The inflection point for the UL_{III}-XANES edge positions were defined and normalized to be 0 eV with the $UO_{2(s)}$ standard and were monitored with $UO_{2(s)}$ before and after each sample. An increase with respect to the relative energy indicates an increase in the average U oxidation state in the sample or standard of interest. Previous studies have shown a linear relationship between the fraction of U(VI) in the solid and the edge position (Bertsch et al. 1994). The spectra were smoothed with the Savitsky-Golay method (Savitsky & Golay 1964).

Experiment 2 – Stirred sediment-water suspensions

Sediment collection and experimental techniques

Evaporation pond sediments from cell 4 of the now drained, Kesterson Reservoir (SJV, CA) were used to make sediment-water suspensions. Sediments were collected from 0 to 0.91 m water depth (0–0.05 m, 0.05–0.20 m, 0.20–0.61 m and 0.61–0.91 m). A composite was made of the samples by adjusting for the mass and scaling to the original horizon thickness. Before scaling, cell 4 sediments contained 3.5 to 8 mg kg^{-1} saturation paste-extractable U (Amrhein et al. 1993). Air-dried sediments were gently ground with a mortar and pestle to pass a 100-mesh sieve. A stirred suspension with a density of 50 g of dry sediment L^{-1} of deionized water was equilibrated with gas mixtures of 5.26 and 0.22 kPa CO_2 (Figure 2). Gas mixtures were obtained using gas cylinders of CO_2 and N_2 attached to a mass-flow controller (Datametrics Model 1605, Edwards High Vacuum Intl., Willmington, MA). The outside of the flask (Figure 2) was covered to limit the growth of photosynthetic organisms. The sediment-water mixture was allowed to "free-drift" from oxidizing to more reducing conditions. One g of dried alfalfa (Wiley Mill-ground, 20 mesh) was added after 18 days of free-drift to enhance microbial reduction. Prior to sampling, the suspension pH and Eh were measured *in situ*. Eh was measured with a Pt redox/calomel reference electrode. Sediment-solution samples of approximately 30 mL were removed from the mixtures, centrifuged, filtered with a 0.45 μm filter, acidified with 0.1 mL of concentrates trace metal (TM) grade HNO_3 and stored at 4 °C prior to analysis. Dissolved U was determined by ICP-MS in 10 g L^{-1} TM HNO_3 with an internal standard of 50 $\mu g\ L^{-1}$ Bi. Dissolved Fe and Mn were determined by inductively-coupled plasma optical emission spectroscopy. Major anions were determined as above. Dissolved organic carbon (DOC) was measured with a Dohrmann C analyzer.

Geochemical speciation modelling, Experiments 1 and 2

The computer speciation program MINTEQA2 (USEPA 1991) was used to calculate ion activities and mineral saturation indices (SI) for solutions from Expts. 1 and 2, with the Davies Equation. In addition to the major species in solution (Na^+, Ca^{2+}, Mg^{2+}, Cl^-, $SO_4{}^{2-}$, $PO_4{}^{3-}$ and inorganic C) available measured concentrations of Mn as Mn(II), and Fe as Fe(II) were input. Uranium was input as U(VI) because it was determined to be the more common dissolved U species (in the Eh range of +310 to −260 mV) in a similar study, which also used SJV sediments and saline waters (Duff et al. 1997a). Solids were not allowed to precipitate. Thermodynamic data for U species were taken from Grenthe et al. (1992) with the exception of the U(VI)-

Table 2. Experiment 1. Natural and synthetic drainage water (pond inlet water) amended with algae, sucrose, sodium acetate, and alfalfa. The water was inoculated with pond sediment. Values in parentheses pertain to U oxidation state measurements for sediments after 96 hours in air.

Treatment	Water pH	H_2S Smell[1]	% U lost from solution	% Uranium(VI) in sediment
Oxic[2]	8.3	●	—	85
Anoxic[2]	8.2	○	—	73
Algae, Natural	7.2	●	2	83
Algae, Synthetic	7.5	●	10	77
Alfalfa, Natural	6.8	○	95	4.4 (34)
Alfalfa, Synthetic	6.5	○	95	4.0 (48)
Sucrose, Natural	6.7	●	69	75
Sucrose, Synthetic	7.3	●	94	86
Acetate, Natural	7.6	●	20	78
Acetate, Synthetic	7.2	●	1	84

[1] ● No volatile sulfides present by smell; ○ Volatile sulfides present.

[2] Values represent *in situ* measurements of collected sediments from Duff et al. (1997a).

hemicarbonate species $(UO_2)_2CO_3(OH)_3^-$, which was taken from Tripathi (1983).

Results

Experiment 1 – Three week Pond 14 sediment-pond inlet water equilibrations

The natural inlet water was oxic upon collection (Table 1) and the PCO_2 was calculated to be 0.03 atm (or about 3.03 kPa), a level ten-fold greater than that for pure water in equilibrium with atmospheric CO_2 (0.0035 atm or about 0.35 kPa). Geochemical calculations predicted that nearly all of the dissolved U(VI) was present as U(VI)-tricarbonate species. The synthetic water had a lower carbonate alkalinity and ionic strength than the natural water. Uranium speciation in the synthetic water was predicted to be dominated by the U(VI)-tricarbonate (84%) species and small quantities of the U(VI)-di (14%) and -hemicarbonate (2%) species present.

The alfalfa amended pond water had the greatest loss of U from solution of the treatments, with 95% removal (Table 2). Water from these samples smelled of sulfides, indicative of sulfate reduction (SR), and suggesting that reduction of U(VI) to U(IV) had occurred. This was verified using XANES analysis of the solid phase collected by centrifugation (discussed below) that showed 96% of the solid phase U was in a +IV oxidation state.

Significant losses of U also occurred in the sugar amended water samples, with 69% and 94% loss for the natural drainage water and synthetic pond water, respectively. These samples did not have a sulfide smell suggesting that the U loss might not be a result of SR. XANES analysis of the solid phase U from these samples verified that the predominant oxidation state was +VI (Table 2). In these samples 75% and 86% (natural and synthetic waters, respectively) of the solid phase U was in a +VI oxidation state, similar to the natural pond sediments.

Only small losses were observed in the *Chlorella* cultured water with 2% (natural water) and 10% (synthetic water) of the soluble U removed from solution. The low uptake of U by *Chlorella* grown in the drainage water can be attributed to the higher CO_3^{2-} and P concentrations of this water. Nakajima et al. (1979) concluded that the anionic ion pairs that these species form with U(VI) reduce uptake by algae. The algae treatment was aerobic so losses due to U reduction were not expected. These low removal rates were similar to those measured in the acetate-treated water (Table 2). In this case, the U may have been unavailable for reduction due to U-acetate complexation and/or poor growth of anaerobic microorganisms capable of degrading acetate. The solid phase from the algae and acetate treatments had similar U oxidation states; from 73% to 84% of the solid phase U was present in the +VI oxidation state. For a suspension from the alfalfa treatment that was opened to room air for four days, between a third and half of the precipitated U was readily oxidized back from +IV to a +VI oxidation state during this time, showing that the recently formed U(IV) was susceptible to oxidation in air. As mentioned above, the oxidation state of U in the solid phase was determined using XANES spectroscopy. Spectra for the standards are shown in Figure 1. Post-edge multiple resonance features such as a "shoulder" are often observed in U(VI)-XANES spectra (Fargas et al. 1992; Bertsch et al. 1994). The shoulder is usually attributed to the structural coordination environment near the U(VI) atom. The $U(VI)O_2^{2+}$ ion and most U(VI) solids have a coordination number (CN) of six. In contrast, U(IV) in $UO_{2(s)}$ usually has a CN of eight, and does not have a "shoulder."

The algae, sugar and acetate treatments, which were equilibrated in the natural water, all had similar spectral features and edge positions (Figure 3, spectra for synthetic water-sediment treatments not shown). The edge positions were shifted with respect to the normalized value of 0 eV for U(IV) and were used to calculate the relative proportion of U(IV) and U(VI) in the sample. Also, the "shoulder" feature was present for the algae-, sugar-

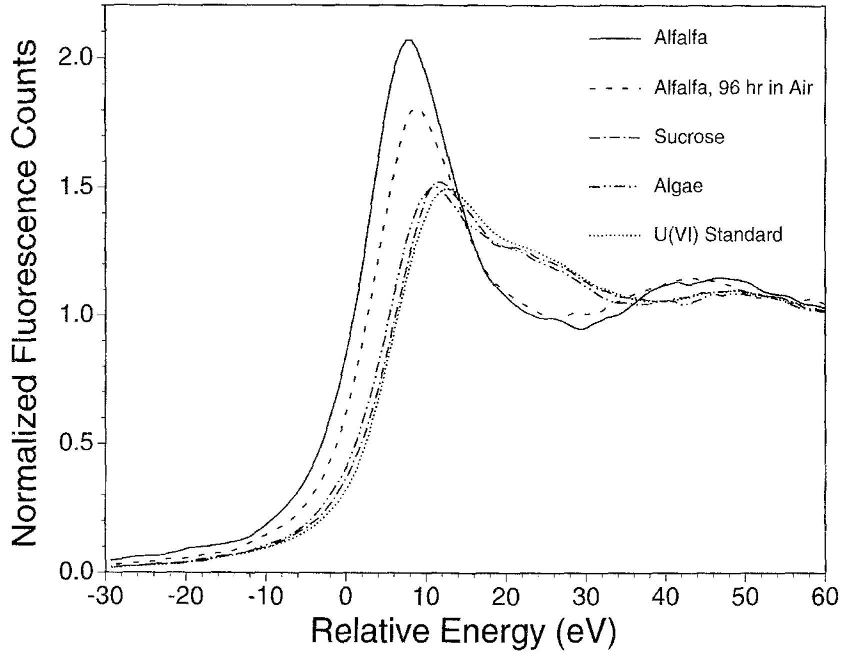

Figure 3. The UL_{III} relative edge position for solid phases from the natural inlet waters collected from Expt. 1 and the reference U(VI) standard. Uranium(VI) was added to the natural pond water to give a concentration of 12 mg U(VI) L^{-1}. The spectrum for the acetate treatment (not shown) closely resembled that of the sucrose treatment. Synthetic treatments (not shown) resembled the natural pond water treatments.

and acetate-treated samples suggesting the U in the samples had a similar coordination environment to that observed for U(VI).

In contrast, the spectrum for the anoxic, alfalfa-treated water had a higher absorption edge and no visible shoulder. There was an increase in the overall U oxidation state in the sediment in the alfalfa-treated sediments after 4 days in air (Figure 3). However, this increase in the edge position did not coincide with the emergence of a shoulder. This suggests the air oxidation of U(IV) did not result in the formation of a U(IV)/(VI) solid with the same coordination environment as the added U(VI). The absence of a shoulder in XANES spectra for *in situ* U in sediments containing predominantly U(VI) was observed (Duff et al. 1997a). The absence of a shoulder feature does not preclude its existence. It may be present in the XANES spectra, but due to the height of the white line (top of the absorption edge) the contribution of a shoulder in the post-edge resonance portion of the spectra may not be resolvable.

Experiment 2 – Stirred sediment-water systems under controlled CO_2

The partial pressure of CO_2 had a significant effect on suspension pH, carbonate alkalinity, and soluble Mn, Fe, and U at all Eh values (Table 3). There was no evidence for sulfate reduction (SR) in these stirred suspensions until fresh OM was added (alfalfa) at 430 hours. Then, in the high CO_2 system, approximately half of the soluble SO_4^{2-} was lost due to SR. Concurrently there was a decrease in soluble U, most likely due to sulfide-induced U reduction as seen in Expt. 1 above. After the addition of OM, the DOC values in the high PCO_2 system increased to 62 mg L^{-1} but then decreased rapidly with decreasing Eh – suggesting that the OM was being utilized in SR. DOC values in the low PCO_2 systems continuously increased after the addition of the OM indicating that the degradation of OM was slow. This was also accompanied by significantly less SR at this higher pH, even though the Eh was somewhat lower (Table 3).

Uranium was 10 to 20 times more soluble in the high PCO_2 system as compared to the low PCO_2 system. This higher solubility is attributed to higher carbonate alkalinity, which promoted the formation of highly soluble U(VI)-carbonate complexes. Earlier studies of U adsorption on soils showed these complexes are not likely to adsorb to negatively-charged sediment surfaces (Duff & Amrhein 1996).

After the addition of OM, dissolved U concentrations decreased due to precipitation as U(IV) and U(IV)/(VI) solids. The U oxides, UO_2 (S.I. of +2.6), U_3O_8 (S.I. +6.6) and U_4O_9 (S.I. of +6.8) were predicted to be oversaturated after 240 hours of equilibration in the high PCO_2 system, and then remain so for the duration of the experiment. The U(VI)-oxyhydroxide solid (schoepite, $UO_3 \cdot 2H_2O$) was highly undersaturated in both systems.

Discussion and conclusions

In the low PCO_2 system, it is likely that sorption processes controlled U solubility. There are examples of U-contaminated waters being treated using biosorption (Tsezos 1990). Uranium(VI) forms strong complexes with OM (Nash et al. 1981) – a likely mechanism for U loss in the algae and microbial systems. In an earlier study with oxidized, calcareous SJV soils at similar carbonate alkalinities and pH values, we reported that sorption was the mechanism controlling U concentrations in solution (Duff & Amrhein 1996).

Microbially-mediated reductive precipitation for *in situ* immobilization of U in contaminated materials has been proposed (Barton et al. 1996; Phillips et al. 1995). Laboratory cultures of anaerobic microorganisms capable of reducing Fe(III) and SO_4^{2-} have been shown to use UO_2^{2+} as a terminal

Table 3. Experiment 2. The total dissolved concentrations of some redox sensitive constituents from the stirred sediment-water equilibration. Alfalfa was added at 430 hours.

Time	Eh	pH	Carbonate Alkalinity	DOC	Mn^{2+}	Fe^{2+}	SO_4^{2-}	U
hr	mV		$mmol_c\ L^{-1}$	$mg\ L^{-1}$				$\mu g\ l^{-1}$
5.26 kPa PCO_2								
0	350	7.2	3.4	26	0.06	93	710	7
8	230	7.1	6.6	29	0.32	111	750	23
24	170	7.0	7.3	40	0.56	132	760	32
72	45	7.0	7.7	27	3.6	130	760	35
96	–10	7.0	7.7	33	4.0	133	770	36
170	–30	7.0	8.2	20	4.4	122	750	40
270	–60	7.0	8.7	13	4.7	158	710	45
340	–120	7.0	8.8	14	4.5	159	710	55
430	–130	7.0	9.0	16	4.5	159	700	42
500	–210	7.1	10.2	62	4.4	195	650	40
600	–220	7.4	14.2	29	3.6	195	460	41
700	–210	7.5	14.8	33	3.2	175	410	29
840	–220	7.5	15.8	25	3.0	180	370	27
0.22 kPa PCO_2								
0	300	8.8	0.4	20	0.1	0.05	720	1
8	210	8.8	0.8	21	0.2	0.03	720	2
24	160	8.8	0.7	17	0.2	0.07	730	5
72	10	8.7	0.9	17	0.3	0.02	740	4
96	–10	8.8	0.8	17	0.4	0.02	740	4
170	–30	8.8	0.8	19	0.4	0.04	740	2
270	–54	8.7	0.7	20	0.5	0.03	720	2
340	–100	8.7	0.7	21	0.5	0.02	730	2
430	–230	8.6	0.8	23	0.5	0.03	720	2
500	–270	8.4	1.6	77	0.5	0.05	710	2
600	–280	8.5	2.0	86	0.4	0.04	660	3
700	–280	8.5	2.2	91	0.4	0.04	630	3
840	–280	8.5	2.4	100	0.3	0.03	620	2

electron acceptor (Gorby & Lovley 1992; Francis et al. 1994; Ganesh et al. 1997). Studies such as these usually conclude that $UO_{2(s)}$ is formed and the studies do not quantify the average oxidation state of U in the solid phase. Pure uraninite is rarely observed in the natural environment, but a variety of reduced U oxides of mixed stoichiometry (containing both U(IV) and U(VI)) are common (Langmuir 1978). Studies on the oxidation of natural and synthetic $UO_{2(s)}$ in air and solution generally conclude that the surface of UO_2 is covered by a partially oxidized coating. This coating which is thought to dissolve rapidly under oxidizing conditions, is removed with strong acid (Sunder et al. 1996; Casas et al. 1994; Finch & Ewing 1992). Once the coating is removed, an *in situ* oxidation step, resulting in the conversion of UO_2 to $UO_{(2+x)}$ (where "x" ≤ 0.33) is followed by the release of U(VI) at the oxide-water interface.

Francis et al. (1994) reported that U(VI) should be reduced at Eh values associated with the occurrence of Mn(IV) reduction and Fe(III) reduction. In this study, we found that both Mn and Fe reduction always occurred before U reduction. Even after SR had begun, U loss from solution lagged behind. A U(IV)-solid, possibly UO_2, only formed under low redox conditions when SR was vigorous. Although microorganisms exist that can directly use U(VI) as a terminal electron acceptor, our results suggest the reduction occurs by direct reaction with sulfide in a high SO_4^{2-} brine.

After 96 hours of exposure to air, partial oxidation of this newly formed U(IV)-solid occurred. This finding shows that *in situ* reductive precipitation of U(VI) to U(IV) is not a permanent method for immobilization of U in these sediments.

Under aerobic and moderately anaerobic conditions, a mixed oxidation state U solid was formed. The ratio of U(IV) to U(VI) was very similar to that measured in natural pond sediments indicating that biosorption followed by OM deposition was the dominant mechanism of U removal in these ponds. In an earlier study of the SJV pond sediments we reported that the U(IV) to U(VI) ratio increased with depth of burial (Duff et al. 1997a), suggesting a slow reduction transformation was occurring. Although SR occurred in these sediments, the microbial activity was not high and no evidence for $UO_{2(s)}$ was found in the sediments. Surprisingly, U(VI) was the dominant insoluble form of U despite low redox conditions.

The reduction of U(VI) is partially dependent on Eh and pH, but may also be a function of limiting nutrients such as N and sorption processes. Despite the smell of sulfides, the untreated anoxic Pond 14 sediments had mostly U(VI). Under nutrient limiting conditions, SR was slow and thus, the rate of U(VI)-reduction was also low. This allowed time for mixed oxidation-state solids of U(VI) and U(IV) to form and oversaturation with $UO_{2(s)}$ was not reached. Additionally, the reduction reaction may have been limited by the complexation of U by OM.

These studies indicate that the reduced U phases in the evaporation ponds can readily oxidize when the pond sediments are disturbed and exposed to air. The reworking of SJV pond sediments by farm managers has been considered as an option to reduce sediment U to more environmentally acceptable levels. However such actions as reworking the pond banks, may promote the oxidation of U(IV) and the subsequent release of elevated levels of U from the sediments during precipitation and flooding events. Findings from this research have potential applications to the management and remediation of redox affected environmental areas that received U-contaminated waters associated with nuclear energy activities, within the U.S. Department of Energy Complex and the former Soviet Union.

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