The influence of citrate and oxalate on $^{99}\text{Tc}^{\text{VII}}$, Cs, Np^{V} and U^{VI} sorption to a Savannah River Site soil

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Abstract

Batch sorption experiments were conducted with 0.5 to 50 ppb ^{99}Tc , ^{133}Cs , ^{237}Np and U in the presence and absence of citrate and/or oxalate in a 25 g/L Savannah River Site (SRS) soil suspension. Citrate and oxalate were the ligands of choice due to their relevancy to plant exudates, the nuclides were selected for their wide range of biogeochemical behavior, and the soil from SRS was selected as a model Department of Energy (DOE) site soil. Batch samples were continually mixed on a rotary shaker and maintained at a pH of approximately 5. Analysis via ICP-MS indicated that sorption of ^{237}Np increased with ligand concentration compared to baseline studies, as did sorption of ^{99}Tc although to a lesser extent. The increased sorption of ^{237}Np is proposed to be due to a combination of factors that are dependent on the ligand(s) present in the specific system including, ligand dissolution of the soil by citrate and formation of tertiary soil-oxalate-Np complexes. The increased ^{99}Tc sorption is attributed to the dissolution of the soil by the ligands, leading to an increase in the number of available sorption sites for ^{99}Tc . Uranium sorption decreased and dissolution of native uranium was also observed with increasing ligand concentration, thought to be a result of the formation of strong U-ligand complexes remaining in the aqueous phase. The majority of these effects were observed at the highest ligand concentrations of 50 mg/L. No notable changes were observed for the ^{133}Cs system which is ascribed to the minimal interaction of Cs^+ with these organic ligands.

Keywords: Technetium; cesium; neptunium; uranium; sorption; ligands

1. Introduction

1.1. Background and motivation

Technetium-99 (^{99}Tc), cesium (^{137}Cs and ^{135}Cs), neptunium-237 (^{237}Np) and uranium (^{238}U , ^{235}U , and ^{234}U) are all present to varying extents in legacy nuclear waste, proposed spent nuclear fuel repositories and in potential fuel reprocessing and recycling streams (Bradbury and Baeyens, 2000; Carlton et al., 1993; Choppin, 2007; Maher et al., 2012; NCRP, 2006; Schulte and Scoppa, 1987). The quantitative distribution of the isotopes is system dependent. For example, all of the listed isotopes are present in legacy waste. Comparatively, whereas ^{99}Tc and ^{137}Cs are of major concern in advanced waste forms resulting from nuclear fuel recycling scenarios, the concentrations of actinides in such waste will be minimal. The selected radionuclides are long-lived risk drivers in the Department of Energy (DOE) complexes and are expected to be mobile and potentially hazardous to human and environmental health. Furthermore, this suite of radionuclides encompasses a broad range of biogeochemical behavior

characterized by different sorption mechanisms, redox activity, solubility, overall mobility and bioavailability, and can thus be used to inform the behavior of similar radionuclides. Of the many DOE complexes, the Savannah River Site (SRS; Aiken, South Carolina) is the location of interest as this study is part of a larger DOE EPSCoR (Experimental Program to Stimulate Competitive Research) initiative in South Carolina. Increased site specific knowledge on the biogeochemical behavior and transport mechanisms of radionuclides (or other contaminants of concern) allows for more appropriate and quantifiable risk assessment development which is pertinent in the management of such contamination in the environment (NCRP, 2006). While this work's intention is not to develop such a risk assessment model, it does provide important insights into mechanisms and factors that affect the environmental mobility of the aforementioned nuclides that may be of importance in the future improvement of appropriate risk management practices.

The overall objective of this work is to gain a conceptual understanding of Tc, Cs, Np and U sorption to SRS soil in the presence and absence of naturally occurring organic ligands via batch sorption experiments in order to elucidate the potential for plant exudates to modify the biogeochemical behavior of these nuclides. The specific objectives of this study include:

- (1) Provide baseline distribution coefficients to give an indication of the expected mobility and solid to aqueous partitioning of each radionuclide.
- (2) Quantify the changes in the biogeochemical behavior of the aforementioned radionuclides in the presence of varying concentrations of naturally occurring plant relevant organic ligands.
- (3) Identify what factors induce a significant impact on mobility in comparison to the baseline results and what mechanisms may be responsible for the changes.

1.1.1. Technetium

Technetium-99 is of particular environmental concern in spent fuel reprocessing and storage due to its relatively high fission yield (~6%), long half-life (2.11×10^5 years) and high mobility in oxic environmental conditions as the pertechnetate ion (TcO_4^-) (Icenhower et al., 2010). Transport of technetium in the environment is governed by complex, coupled biogeochemical processes including redox reactions, complexation with organic exudates, uptake in plants, and sorption to mineral surfaces (Icenhower et al., 2010; Schulte and Scoppa, 1987). Technetium is predominantly found in the environment as pertechnetate, which is very weakly complexing and thus highly mobile with very low, sometimes even negative, distribution coefficient (K_d) values reported in literature (Icenhower et al., 2010; Kaplan et al., 2008). The minimal sorption is explained by the predominance of negative surface charge on sediments, which repel the anionic pertechnetate (Icenhower et al., 2010). However, there is potential for ligand (e.g., plant exudate) facilitated decrease in mobility if (1) Tc^{VII} is reduced to Tc^{IV} , (2) if complexation reactions occur with the ligands, or (3) if ligand facilitated disturbances of soil particles

exposes more viable sorption sites on the mineral surfaces (Icenhower et al., 2010; Liu et al., 2012). Oxic conditions are expected to be maintained throughout this work, so ^{99}Tc is expected to persist in the system as the weakly interacting pertechnetate ion. Alterations to the soil will become an increasingly important factor affecting the sorption behavior of ^{99}Tc .

1.1.2. Cesium

Cesium-137 exists as a monovalent cation (Cs^+) in natural waters and is a contaminant of concern and risk driver at former nuclear materials processing facilities, such as SRS, due to its relatively long half-life (~30 years) and its relative abundance in legacy radiological waste (Zaunbrecher et al., 2015). With a much longer half-life, ^{135}Cs ($t_{1/2} = 2.3$ million years) is a potential risk driver for longer-term disposition of spent nuclear fuel or waste forms from reprocessing. A wide range of factors can influence the type and extent of Cs sorption and mobility in a system, including soil mineralogy, clay content, cation exchange capacity, concentration of Cs, presence of competing cations, moisture content, pH, ionic strength, etc. (Bostick et al., 2002; Goto et al., 2014; NCRP, 2006; Zaunbrecher et al., 2015b). The initial aqueous concentration of Cs in the system impacts the distribution coefficient by dictating the exchange site it will sorb to and how reversible that sorption process is with respect to competing ions (Bostick et al., 2002; Bradbury & Baeyens, 2000). Strong absorption to many types of clay is characteristic of Cs (Goto et al., 2008). Hydroxy-interlayered vermiculite (HIV) and kaolinite are the dominant clays in SRS soil, and the former has been attributed as the major sorption site for Cs in SRS soil (Goto et al., 2014; Zaunbrecher et al., 2015b). In particular, Cs exhibits a strong selectivity for the fairly limited HIV interlayer wedge sites (Goto et al., 2014; Zaunbrecher et al., 2015b). Cesium is held strongly in these HIV sites which govern the cation-exchange capacity of the SRS and can become strongly fixed to these sites over time (Goto et al., 2014; Zaunbrecher et al., 2015b). Goto et al. (2008) reported concentration dependent K_d values for various SRS soils ranging from 4.7 – 1460 L/kg for slightly acidic samples (pH of 4.12 to 4.92 closest to the conditions of this study), the majority of the K_d values were around or below 100 L/kg, apart from the very low cesium concentration samples. Due to the moderately strong sorption to the HIV grains present in SRS soils, Cs is expected to exhibit limited mobility in the subsurface, although its presence in pore water yields the potential for biological uptake (Bostick et al., 2002; NCRP, 2006; Zaunbrecher et al., 2015b).

1.1.3. Neptunium

The long half-life (2.14×10^6 years) and high mobility in oxic conditions as the pentavalent neptunyl ion ($\text{Np}^{\text{V}}\text{O}_2^+$) make ^{237}Np an environmental concern. Even with the relatively low yield (0.03%) of ^{237}Np in spent fuels initially, the long half-life of ^{237}Np results in its dominance after 100,000 years (Kaszuba and Runde, 1999). The presence of Np as $\text{Np}^{\text{V}}\text{O}_2^+$ under environmental conditions indicates that Np, similar to Tc, will be weakly complexing, and resistant to hydrolysis due to its relatively low effective charge

compared to actinides of other (III, IV and VI) oxidation states (Choppin, 2007). Studies on similar SRS soils have resulted in distribution coefficient (K_d) values of 4.26-9.05 L/kg (Miller, 2010). Law et al. reported microbial mediated reduction of Np^{V} to Np^{IV} results in increased complexation and sorption to minerals, with reported slow ability to reoxidize and remobilize after reduction (2010). Generally sorption of $\text{Np}(\text{V})$ to mineral surfaces will increase with increasing pH; however, several studies have found that complexation of $\text{Np}(\text{V})$ with carbonate and natural organic matter can decrease sorption at high pH values (Arai et al., 2007; Girvin et al., 1991; Kohler et al., 1999; Li & Tao, 2003; Schmeide & Bernhard, 2010). Under the oxic conditions of this study, neptunium is expected to persist in the pentavalent state. Geochemical speciation modeling discussed below shows that neptunium will persist as the free NpO_2^+ ion as well as $\text{Np}(\text{V})$ -citrate and $\text{Np}(\text{V})$ -oxalate complexes. Thus, the influence of changes in neptunium chemical speciation on sorption to SRS soil will be examined in this work.

1.1.4. Uranium

The ubiquitous presence and high relative quantity of uranium in legacy nuclear waste, spent nuclear fuel, uranium or nuclear material processing facilities, and proposed nuclear fuel repositories dictates that it is a major nuclide of concern in the environment (Choppin, 2007; Dong and Wan, 2014; Maher et al., 2012). Uranium is found in the hexavalent state in aqueous oxic environmental conditions as the uranyl ion ($\text{U}^{\text{VI}}\text{O}_2^{2+}$) with high solubility and mobility (Morss et al., 2010). Its presence in the hexavalent state dictates that it undergoes hydrolysis above pH of about 3 and exhibits a relatively high complexation affinity with many ligands (compared to Np^{V} and Tc^{VII}) including carbonate, citrate, and oxalate (Clark et al., 1995; Morss et al., 2010). Additionally, U^{VI} also readily sorbs to mineral surfaces resulting in comparatively high K_d values, substantially greater than those for the other nuclides in this study. Uranium is also present in the tetravalent oxidation state under reducing conditions corresponding with a low solubility, producing precipitates such as uraninite (UO_2) (Maher et al., 2012). Formation of $\text{U}(\text{VI})$ complexes with carbonate, citrate, and oxalate change the formal charge of the uranyl ion and minimize sorption to mineral surfaces at circumneutral pH values as neutral or negatively charged U:ligand complexes partition to the aqueous phase (Alliot et al., 2005; Kohler et al., 2004; Lenhart & Honeyman, 1999; Murphy et al., 1999). Under the conditions of this work, the hexavalent UO_2^{2+} ion is expected to persist and $\text{U}(\text{VI})$ -citrate and $\text{U}(\text{VI})$ -oxalate complexes will form based on the U:ligand molar ratios as discussed below.

1.1.5. Ligands/exudates

Several transition metals such as iron (Fe), zinc (Zn), manganese (Mn) and copper (Cu), are essential for the normal physiology of plants, as they serve as cofactors for many key enzymes involved both in carbon and nitrogen metabolism and are vital for the normal functioning of mitochondria and plastids (Romheld and Marschner, 1991). However, the bioavailability of these transition metals in most soils is typically

orders of magnitude lower than plant needs (Schmidt, 1999). For example, iron, though the fourth most abundant element in the Earth's crust, is the third most limiting nutrient for plant growth, due to its limited solubility (Lindsay and Schwab, 1982; Schmidt, 1999). Hence, plants rely on elaborate strategies, with multiple layers of redundancy, for the uptake of metal nutrients from soils (Curie and Briat, 2003). During most forms of nutrient stress, roots actively or passively release significant amounts of cellular metabolites into the rhizosphere (Bais et al., 2003). These rhizodeposits are comprised of complex mixtures of carbohydrates, amino acids, organic acids, phenolic compounds, fatty acids, sterols, vitamins, enzymes, purines/nucleosides as well as inorganic ions, gaseous molecules and root border cells all of which influence the acquisition of mineral nutrients (Dakora and Phillips, 2002). Sugars, amino acids, and organic acids are thought to be the major components of root exudates (Farrar et al., 2003). Organic acids directly facilitate the dissolution of metal nutrients from the insoluble mineral phase (Jones and Darrah, 1994), while amino acids and sugars indirectly affect plant nutrition by increasing microbial metabolism in the rhizosphere (Farrar et al., 2003). In soil, the reaction of organic acids with different metals depends on many factors including solid phase sorption/desorption, diffusion rates, hydrolysis, and microbial degradation. Citric and oxalic acids, the intermediaries of the energy generating tricarboxylic acid cycle, are the major components of most root exudates, especially in plants that experience micronutrient stress. For example, enhanced secretion of citrate has been reported for various plants encountering Fe deficiency, consequently forming Fe complexes that are readily absorbed by roots (Jones et al., 1996). Apart from increasing the bioavailability of metals, these organic acids could also decrease the metal toxicity through complexation reactions (Osawa and Kojima, 2006). Organic compounds in root exudates such as organic acids, alcohols, phenols and proteins may also function as carbon and nitrogen sources for microorganisms capable of degrading organic contaminants (Salt et al., 1998). Hence, root exudates play a fundamental role in the mobility and availability of metal ions through diverse mechanisms.

1.2. Working Hypothesis

Ligands interact with soil surfaces and/or aqueous metal ions via various mechanisms potentially leading to alteration of the normally observed metal ion sorption in the absence of ligands (Parks, 1990; Schindler, 1990; Stumm, 1992). The general interactions of the ligand coupled with the particular geochemical behavior unique to each analyte ion will dictate the overall effect on sorption in the presence of the ligand amendment. Among the factors that dictate an ion's interaction probability, the effective charge of the ion is fundamental to the prediction of ion interaction. For example, the hexavalent UO_2^{2+} , with the highest effective charge in this suite of ions, is expected sorb strongly to surfaces and have comparatively high complexation affinity. Whereas, TcO_4^- is expected to behave in a contrasting manner resulting in minimal sorption and low complexation affinity. Cs^+ and NpO_2^+ are expected to behave in less extreme manners, with Cs^+ exhibiting a higher sorption affinity as compared to NpO_2^+ .

Three notable processes are hypothesized to be the main means of interaction between the ligands (citrate and/or oxalate) and the other components in the system, i.e. the analyte ($^{99}\text{TcO}_4^-$, $^{133}\text{Cs}^+$, $^{237}\text{NpO}_2^+$ and UO_2^{2+}) and/or Savannah River Site soil, leading to changes in observed metal sorption:

- (1) Ligand-metal analyte aqueous complexation, L-M complexes (Stumm & Morgan, 1996).
Formation of L-M complexes will effectively decrease the sorption of the analyte to the soil surface as the L-M complex remains in the aqueous phase. This will be most probable for metal ions with an inherently strong sorption affinity; in this case UO_2^{2+} is expected to be affected by this type of ligand interaction if the ligand-uranyl complex outcompetes the sorption of UO_2^{2+} to the soil surfaces.
- (2) Formation of type B ternary complexes between the soil surface, polydentate ligand and metal analyte, S-L-M complexes (Schindler, 1990; Stumm, 1992). Type B ternary complexes will result in increased sorption of the analyte to the soil surface for those analytes that would otherwise weakly sorb in absence of complexing ligands. The likely candidate for effects due to this type of interaction is NpO_2^+ as it is a weakly sorbing ion in general, mainly staying in the aqueous phase in the absence of chelating ligands and weakly complexes with the ligands when present.
- (3) Ligand promoted dissolution of mineral surfaces of the soil, similar to that described by Stumm (1992). This dissolution or mineral surface disturbance will lead to an increase in sorption due to a greater available surface area as the particle size of the solids decrease (Parks, 1990). An increased reactive surface area could also be the result of disaggregation of smaller particles and the dispersion of surface coatings of larger mineral grains. The increased sorption resulting from this mechanism is an indirect effect of the ligand interacting with the soil surfaces and particles as compared to a direct effect on the metal analyte ion as described in hypothesis (1) and (2). This type of ligand interaction will most likely induce a sorption increase for ions that are normally weakly sorbing or complexing such as, TcO_4^- and NpO_2^+ as more sorption sites become available.

2. Materials and Methods

2.1. Batch sorption methods

The soil samples used in this study were taken from SRS's West Borrow Pit, the properties are summarized in Table 1. The surface area was determined using $N_2(g)$ adsorption on a Micrometrics ASAP 2020. Potentiometric titrations of the SRS soil were performed in 50 g/L soil suspensions in 0.01 M, 0.05 M, and 0.1 M NaCl using a Metrohm 836 Titrando. Cation exchange capacity (CEC) and acidity were determined by Mehlich extraction by Clemson University's Agriculture Service Laboratory. Extractable Fe and Al was determined by citrate-bicarbonate-dithionite (CBD) extraction (Loeppert and Inskeep, 1996) and organic matter content was determined by loss on ignition (Nelson and Sommers, 1996). The particle size was determined using a standard hydrometer method (Gee and Bauder, 1996).

Table 1: Chemical and physical characteristics of the SRS soil

Property	Measurement
Surface Area	14.1 m ² /g
pH (50/50 soil/water)	4.76
Point of zero charge	4.9
Sand/Silt/Clay (%)	66/14/20
Organic matter	0.90%
CEC	3.3 meq/100g
Acidity	2.4 meq/100g
CBD extractable Fe	6.01 ± 0.68 mg/g
CBD extractable Al	1.98 ± 0.20 mg/g

The soil properties listed in Table 1 indicate this is a sandy clay loam. The relatively low organic matter content necessitated addition of organic ligands to simulate plant exudates. The CEC is relatively low but contains sufficient capacity to facilitate sorption of trace level radioisotopes such as ^{137}Cs . The moderate surface area and extractable Fe and Al content indicate there are reactive surfaces capable of binding relatively strongly sorbing ions such as NpO_2^+ and UO_2^{+2} . The low pH indicates a net negative surface charge will develop at circumneutral pH values which will enhance sorption of cations via increased electrostatic attraction. Each of these processes and properties along with the influences on radionuclide sorption will be discussed below.

A stock solution containing 100 ppb each of ^{133}Cs (a stable analog for ^{137}Cs and ^{135}Cs ; High-Purity Standards, Charleston, SC), ^{237}Np (Eckert & Ziegler Isotope Products, Valencia, CA), ^{99}Tc (Eckert & Ziegler Isotope Products, Valencia, CA) and U (High-Purity Standards, Charleston, SC) was prepared in a background electrolyte solution of 0.01 M sodium chloride (NaCl). The radionuclide stock solution was then adjusted to a pH value of 5 by adding small volumes of 0.1 M HCl or 0.1M NaOH. Three ligand stock solutions were prepared containing citrate, oxalate and a mixture of citrate and oxalate at concentrations of 100 mg/L each for all solutions. The citrate stock solutions were prepared using sodium citrate dihydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$; Fisher Scientific) and the oxalate stock solutions were prepared using oxalic acid dihydrate ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; J. T. Baker). All three stock ligand solutions were prepared in a background electrolyte solution of 0.01 M NaCl and pH adjusted to 5 using the same method described previously. The background electrolyte solution of 0.01 M NaCl used in the preparation of the radionuclide and ligand stock solutions was selected in order to closely mimic natural conditions at SRS.

In order to examine the influence of organic ligands on radionuclide sorption to SRS soil an experimental matrix was developed to vary ligand (0.5, 5, and 50 mg/L) and radionuclide concentration (0.5, 5, and 50 ppb (or $\mu\text{g/L}$)) such that a matrix of nine samples were prepared from each ligand stock solution (citrate, oxalate and citrate/oxalate mixture) for a total of 27 ligand batch samples. This experimental matrix ensured each combination of radionuclide and ligand concentrations would be achieved in order to fully understand how each variable would influence the final result. A smaller subset of the experimental matrix of five samples for each ligand group were prepared as control samples without soil to determine if sorption to the walls of the centrifuge tubes had an influence for any of the radionuclides. The baseline batch set, without ligands, was prepared in triplicate to ensure a proper reference for comparison for a total of nine baseline batch samples.

Batch experiments were performed in 15 mL polypropylene centrifuge tubes with 0.25 g of SRS soil to 10 mL of aqueous solution to produce 25 g/L soil suspension. The aqueous phase consisted of a mixture of 0.01 M NaCl background solution, radionuclide stock solution and ligand stock solution for the ligand batch sets or 0.01 M NaCl background solution and radionuclide stock solution for the baseline batch sets. Stock solution additions were carefully pipetted to achieve the desired concentrations defined in the experimental matrix, all additions were monitored gravimetrically.

After initial sample preparation, all samples were pH adjusted as needed to a pH of 5 and placed on an end-over-end rotating mixer. Sampling events at one, three and ten days of mixing were completed by removing a 1.3 mL homogeneous aliquot from each batch tube and centrifuging the aliquot for 20 minutes at 8000 rpm. After centrifugation 1 mL of the centrifuged supernatant was diluted with 9 mL of 2% nitric

acid (HNO₃) in preparation for analysis by inductively coupled plasma mass spectrometry (ICP-MS). After each sampling event and every day between the sampling events the pH of each sample was measured and re-adjusted if necessary to a pH of 5 in order to maintain a constant pH throughout the experiment. Data for the ten day sampling event was used in calculations and reported herein, one and three day sampling data was monitored to verify the samples had reached equilibrium by the day ten sampling event.

Analysis, via ICP-MS, of samples collected and prepared at each sampling event was performed to determine the aqueous concentration of all four analytes in each sample. With knowledge of the initial aqueous concentration and the newly measured aqueous concentration, the concentration of nuclide sorbed to the soil could be determined using the following equations. Equations are written for Np as an example but specific calculations were performed for each nuclide. The sediment concentration of Np ($\mu\text{g}_{\text{Np}}/\text{kg}_{\text{sediment}}$) was calculated using the following equation:

(1)

Where: $[\text{Np}]_{\text{aqu},o}$: Initial aqueous Np concentration (ppb, $\mu\text{g}/\text{L}$)
 $[\text{Np}]_{\text{aqu}}$: Equilibrated (ICP-MS measured) aqueous Np concentration (ppb, $\mu\text{g}/\text{L}$)
 $[\text{Np}]_{\text{sed}}$: Equilibrated sediment Np concentration (ppb, $\mu\text{g}/\text{kg}$)
 V_L : Sample liquid volume, mL
 m_{sed} : Sample sediment mass, g

The sediment water partitioning constant, K_d (mL/g), was calculated via the following equation:

(2)

The percent of Np sorbed was calculated via the following equation:

(3)

The K_d equation (Equation (2)) is numerically equivalent to the traditional K_d equation proposed in ASTM D4646 which has been used in previous sorption tests (ASTM, 2003; Kaplan, 2009). The changes observed in the K_d for each analyte were correlated with the influence the organic ligands, citrate and oxalate, had on the sorption of ¹³³Cs, ²³⁷Np, ⁹⁹Tc and U to SRS soils.

2.2. Sequential Extraction Methodology

Sequential extraction was used to compare the leaching behavior of native Cs, Th, and U in the soil. It is important to note that no additional Cs, Th, or U was added to these soils. Therefore, these sequential extraction data give information on the long term sequestration of Cs, Th, and U in soils. These data

provide a comparison of the long-term equilibrium state of Cs and U relative to the short term batch sorption experiments of this work. Two extraction procedures, mBCR and Tessier, were used for comparison (Rauret et al., 1999; Tessier et al., 1979). The mBCR procedure is a modified method of the Standards, Methods, and Testing Program (formerly Bureau Commune de Reference, BCR) of the European Commission. The fractions for the mBCR procedure are exchangeable, reducible and oxidizable respectively, in order of decreasing mobility. The fractions for the Tessier procedure are exchangeable, bound to carbonates, bound to iron and manganese oxides, bound to organic matter and residual fractions respectively, in order of decreasing mobility. Each of the extraction steps are described below. Samples were rinsed with distilled deionized water between each extraction step. In all cases a one gram aliquot of soil was carried through the extraction procedure and samples were prepared in triplicate. The reported uncertainties below are the standard deviation of triplicate measurements.

2.2.1. Tessier Method

1. The exchangeable fraction used 8 mL of 1.0 M magnesium chloride to extract the most mobile metal ions from the soil. These metals are sorbed to the surfaces of the soil, and are most readily bioavailable to the environment.
2. The bound to carbonates fraction used 8 mL of 1.0 M sodium acetate at pH 5. The metals in this fraction are susceptible to a change in pH (acidic solution). The metals in this phase are less mobile and are less readily available than the metals in the exchangeable fraction.
3. The bound to iron and manganese oxides fraction used 20 mL of 0.04 M hydroxylamine in 25% v/v acetic acid with a pH of 2. The metals in this fraction are susceptible to reducing conditions and are less mobile than the metals in the bound to carbonates fraction.
4. The bound to organic matter fraction used 3 mL of 0.02 hydrogen peroxide to decompose organic matter and 5 ml of 3.2 M ammonium acetate to induce oxidizing conditions necessary for metal extraction. These metals are released from decomposed organic matter and are less mobile than the metals in the bound to iron and manganese fraction.
5. The residuals fraction used 4 mL of perchloric acid and 20 mL of hydrofluoric acid to destroy crystal lattices and fully digest the soil sample. The metals in this fraction are assumed to be immobile and are not bio-available.

2.2.2. mBCR Method

1. The exchangeable fraction used 40 mL of 0.11 M acetic acid to extract the most mobile metal ions from the soil.
2. The reducible fraction used 40 mL of 0.5 M hydroxylamine hydrochloride at pH of 1.5. The metals in this fraction are susceptible to a change in pH (acidic solution) and reducing conditions.

The metals in this phase are less mobile and are less readily available than the metals in the exchangeable fraction.

3. The oxidizable fraction used hydrogen peroxide to decompose organic matter and 50ml of 1 M ammonium acetate to induce oxidizing conditions necessary for metal extraction. These metals are released from decomposed organic matter and are less mobile than the metals in the reducible fraction.

3. Results and Discussion

3.1. Geochemical Speciation Modeling

As one of the critical elements of this study is to quantify the influence of citrate and oxalate on radionuclide sorption to SRS soil, simulations of each radionuclide-ligand system were performed to determine the aqueous species of each radionuclide present in each case. Simulations were performed using Geochemist workbench v8 using the LLNL thermochemical database (Delany and Lundeen, 1990). The exact concentrations of radionuclides and ligands used in the experimental portion of this work were used in the simulations. Even the highest concentrations of citrate and oxalate used in this work were not sufficient to form complexes with cesium and will not form complexes with technetium. Thus, Cs^+ and TcO_4^- are expected to persist. However, there were significant changes in uranyl and neptunyl speciation with changing ligand concentrations. Formation of $\text{NpO}_2(\text{C}_2\text{O}_4)^-$ and $\text{NpO}_2(\text{C}_2\text{O}_4)_2^{3-}$ complexes increased as the oxalate concentration increased (Figure 1(a)) and this was coincident with the decrease in the concentration of free NpO_2^+ . The 1:2 complex $\text{NpO}_2(\text{C}_2\text{O}_4)_2^{3-}$ formation is limited until the concentration of oxalate is at the highest level. Formation of $\text{NpO}_2(\text{citrate})_2^{2-}$ complexes were limited in the mixed Np-citrate-oxalate simulations and were limited to less than 5% in the binary Np-citrate simulations. Thus, in the combined oxalate-citrate-neptunyl system, the Np-oxalate complexes and the free NpO_2^+ ion persisted. Similar behavior was observed for the uranyl system though there was a greater extent of $\text{UO}_2(\text{citrate})^-$ and $\text{UO}_2(\text{C}_2\text{O}_4)_2^{2-}$ formation as compared with similar neptunyl complexes (Figure 1(b)). Formation of these metal-ligand complexes is hypothesized to influence the extent of Np(V) and U(VI) sorption as discussed in the hypotheses above. Such speciation analysis is used in the results and discussion section below to infer the influence of changes in speciation on radionuclide sorption.

(a)

(b)

Figure 1: Geochemical speciation simulations of Np(V) (a) and U(VI) (b) in the presence of both oxalate and citrate simultaneously at pH 4.8 in 10 mM NaCl. Citrate and oxalate concentrations are listed in the legend. Simulation performed using Geochemist Workbench v8 and the thermo.com.V8.R6+ database (Delany and Lundeen, 1990).

3.2. Sequential Extraction Data

The sequential extraction data from the mBCR and Tessier procedures are shown in Figure 2. These data indicate a complimentary nature of the sequential extraction techniques. The most notable difference is greatly increased extraction of all ions using the Tessier method compared with mBCR. Cs partitioning is primarily in the exchangeable and residual fractions of the Tessier method. Both uranium and thorium are most strongly found in the “residual” fraction though low concentrations are leached into all phases. The observation of the majority of native Cs, Th, and U in the “residual” fraction of the Tessier method indicates the potential for an aging process through which these elements become more strongly bound to the soil matrix with time. This is particularly notable for Cs which is expected to bind to mineral surfaces

via ion exchange and would be expected in the “exchangeable” fraction. As discussed below, Cs exhibits relatively weak sorption and the K_d values decrease with increasing total Cs concentration. Furthermore, previous studies have demonstrated that Cs primarily sorbs via ion exchange and thus is expected to be found within the exchangeable fraction (Goto et al., 2014; Zaunbrecher et al., 2015b). The second largest pool of Cs is found in the exchangeable fraction and the largest pool is in the residual fraction. This change from the labile exchangeable fraction to the relatively recalcitrant residual fraction is hypothesized to be due to Cs migration into clay layers as previously observed for mica (Brouwer et al., 1983; Comans and Hockley, 1992; Sawhney, 1972; Zachara et al., 2002; Zaunbrecher et al., 2015a). This soil is dominated by kaolinite clays with <5% smectite/illite clay phases. Migration of Cs into clay interlayers has been demonstrated for 2:1 clays phases and, though there is a relatively low concentration of these phases in this SRS soil, even a small fraction would be sufficient for sorption of the relatively low Cs concentration used in these experiments (Goto et al., 2014; Zaunbrecher et al., 2015b).

Iron occurred at the highest concentrations of all analytes measured and was present in all leached fractions. Previous studies have shown strong sorption of uranium to iron oxide phases (Bargar et al., 2000; Dong and Wan, 2014; Giammar and Hering, 2001; Lenhart and Honeyman, 1999; Payne et al., 1998; Waite et al., 1994). Therefore, it is expected these phases will be the dominant sorption sites for uranium. This is consistent with the sequential extraction data where the largest pools of iron and uranium are found in the Fe/Mn oxide extraction and residual fraction of the Tessier method. A similar correlation was not observed for the mBCR extraction. The largest pool of iron was found in the reducible and oxidizable fractions. This is likely due to reduction of Fe(III) to more soluble Fe(II) by hydroxylamine hydrochloride in the reducible fraction and complexation of iron with acetate (which is present at a higher concentration in the oxidizable fraction relative to the exchangeable fraction). Additionally, uranium is expected to become more strongly sorbed upon reduction thus, the largest pool of uranium is found in the oxidizable fraction. The observation of correlated partitioning of iron and uranium in the sequential extraction data indicates that the sorption behavior discussed below can be described as a competition between uranium complexation with oxalate and citrate and uranium sorption to iron oxide mineral phases.

Figure 2: Selected results from mBCR (top) and Tessier (bottom) sequential extraction studies.

3.3. Baseline K_d values

The average distribution coefficients for the baseline experiments (no ligand present) were found to be within ranges previously reported for similar soils (Table 2). Two values are shown for uranium because non-linear sorption was observed, with higher K_d values associated with samples having initial concentrations of 5 ppb and 50 ppb. The general sorption trend follows what is expected based on the effective charge of the ion, ion size, complexation affinity and the predominance of negatively charged surface sites for the sediment with $\text{UO}_2^{2+} \gg \text{Cs}^+ > \text{NpO}_2^+ > \text{TcO}_4^-$.

Table 2: Average baseline distribution coefficients.

Nuclide	Average K_d (mL/g)	SD	Minimum	Maximum	Range from previous studies
^{99}Tc	-0.2	0.9	-3.0	1.1	-2.9 – 11.2 ^a
^{133}Cs	108	72	4	245	4.7 – 1460 ^b
^{237}Np	5.5	1.8	2.3	7.7	4.26 – 9.05 ^c
^{238}U (low)	813	33	785	849	1.2 – 34,000 ^d
^{238}U (high)	3476	176	3324	3744	

^a(Kaplan et al., 2008) ^b(Goto et al., 2008) ^c(Miller, 2010) ^d(Serkiz and Johnson, 1994).

3.4. Ligand effects on soil

Increasing the ligand concentration resulted in greater dispersion of the soil suspension in which the clay portion of the soil stayed suspended for longer. This is proposed to be due to disaggregation of the particles and development of a net repulsive surface charge. Although limited, particle size analysis on select samples suggests that only the 50mgC/L citrate or citrate/oxalate samples were correlated with smaller particle sizes (<1000nm) in comparison to 0.5 mgC/L. SEM investigation into the effects of ligand concentration on the soil show that the clay fraction appears to be removed from the silicate sand grains when exposed to higher ligand concentrations (Figure 3). This dissolution of the clay portion of the sediment has the potential to impact the sorption and mobility of the radionuclides in question by either exposing more available surface sites for sorption or allowing for leaching of native uranium from the soil.

Figure 3: SEM images of a silicate sand grain from a 0.01 M NaCl, 25 g/L SRS soil solution with (a) 0.5 mgC/L each of citrate and oxalate and (b) 50 mgC/L each of citrate and oxalate. The grain with the higher

ligand concentration (b) is stripped of the clay coating seen on the silicate grain in presence of low ligand concentration (a).

3.5. Technetium

The distribution coefficients for ^{99}Tc and SRS soil with varying concentrations of citrate and oxalate are shown in Figure 4. The presence of 50 mgC/L generally resulted in slightly increased sorption of technetium to SRS soil. The maximum baseline ^{99}Tc K_d value from these studies was 1.1 mL/g (Table 2). In comparison, the citrate/oxalate mixture (Figure 4(c)) produced the greatest increase in K_d values (maximum K_d of 4.3 mL/g). Citrate and oxalate alone (Figure 4(a) and (b) respectively) also resulted in higher sorption for the highest ligand concentrations, to a lesser degree than the combination of ligands, with maximum K_d values of 2.6 and 2.8 mL/g, respectively. Lower concentrations of citrate and/or oxalate did not result in any substantial departures from baseline values with the exception of one anomolous low value for citrate at 5 mgC/L and 5 ppb ^{99}Tc (Figure 4(a)).

(a)

(b)

(c)

Figure 4: Distribution coefficients for ^{99}Tc with SRS soil at baseline conditions (0 mgC/L) and in the presence of varying concentrations (0.5, 5, and 50 mgC/L) of (a) citrate, (b) oxalate, and (c) citrate/oxalate mixture. The citrate/oxalate mixture samples contain 0.5, 5 or 50 mgC/L of each ligand.

The primary mechanism resulting in the increased sorption observed for ^{99}Tc with increasing ligand concentration is proposed to be an indirect effect due to the soil disturbances caused by the ligands. Based on the point of zero charge of 4.9, the SRS soil is expected to have mostly neutral or negative surface sites at pH of 5. Therefore, the anionic pertechnetate sorbs very weakly to it. The slight increase in sorption at higher ligand concentrations can be attributed to the increase in exposed mineral surface area and sorption sites due to the ligand facilitated disaggregation of the soil particles. Visual observations and dynamic light scattering measurements have indicated that the soil particles become more dispersed with increasing ligand concentration. The resulting decrease in particle size aggregates is proposed to yield a greater amount of reactive surface area which causes an increase in Tc sorption. This phenomena is consistent with working hypothesis (3).

Working hypothesis (1) and (2) are not supported for ^{99}Tc . Since technetium is present as the very weakly interacting pertechnetate, it is not expected to form L-M complexes with the citrate or oxalate, both of

which are anionic at the pH used for this study. This expectation coupled with the experimental observation that sorption of ^{99}Tc increases with an increase in ligand concentration, versus decreasing, leads to the dismissal of working hypothesis (1). Additionally, the inability of ^{99}Tc to complex with citrate or oxalate alone also indicates that a tertiary complex is not expected to form, refuting working hypothesis (2) for ^{99}Tc .

3.6. Cesium

Distribution coefficients calculated for ^{133}Cs in the presence of citrate, oxalate and a mixture of both citrate and oxalate can be seen in Figure 5 along with baseline distribution coefficients. All three ligand-radionuclide systems exhibit the same behavior and show no influence of ligand concentration on the distribution coefficients. These results are consistent with the preliminary simulations performed in Geochemists Workbench which showed no Cs-ligand complexes forming at even the highest ligand concentrations. Differences in the distribution coefficients seen in Figure 5 can be attributed to an initial ^{133}Cs concentration dependence which is consistent with the ion exchange model of Cs sorption (Bostick et al., 2002; Bradbury and Baeyens, 2000; Zaunbrecher et al., 2015b). These results show no influence of the presence of ligands or the concentration of ligands on the distribution coefficient of ^{133}Cs in SRS soils as compared to baseline values presented in Table 2.

(a)

(b)

(c)

Figure 5: Distribution coefficients for ^{133}Cs with SRS soil at baseline conditions (0 mgC/L) and in the presence of varying concentrations (0.5, 5, and 50 mgC/L) of (a) citrate, (b) oxalate and (c) citrate/oxalate mixture. The citrate/oxalate mixture samples contain 0.5, 5 or 50 mgC/L of each ligand.

3.7. Neptunium

Citrate alone induced the greatest effect on sorption of ^{237}Np at high citrate concentrations with a maximum K_d value of 476 mL/g for the 50 mgC/L, 0.5 ppb ^{237}Np sample compared to baseline values between 4.4 and 6.7 mL/g; less drastic effects were observed for higher ^{237}Np concentrations (Figure 6(a)). The use of oxalate alone had a much less extreme effect compared to the use of citrate. In the oxalate only system the K_d approximately doubled between the baseline and 50 mgC/L values for all ^{237}Np concentrations with a maximum value of 13 mL/g (Figure 6(b)). The citrate/oxalate mixture produced similar results to the citrate experiment, but to a lesser extent, with a maximum K_d of 168 mL/g (Figure 6(c)).

(a)

(b)

(c)

Figure 6: Distribution coefficients for ^{237}Np with SRS soil at baseline conditions (0 mgC/L) and in the presence of varying concentrations (0.5, 5, and 50 mgC/L) of (a) citrate, (b) oxalate and (c) citrate/oxalate mixture. The citrate/oxalate mixture samples contain 0.5, 5 or 50 mgC/L of each ligand.

Geochemist Workbench models presented in section 3.1 show that $^{237}\text{Np}^{\text{VO}_2^+}$ complexes very weakly with citrate but it has a greater affinity for complexation with oxalate. The complexation of ^{237}Np increases with increasing oxalate concentration ranging from 8% to 91% of the total aqueous ^{237}Np being complexed with oxalate at 0.5 mgC/L to 50 mgC/L respectively. This differing complexation affinity between ligands for ^{237}Np along with the experimental results (Figure 6) suggest support of several of the presented working hypothesis.

3.7.1. *Neptunium and Citrate*

The weak complexation affinity of ^{237}Np with citrate indicates that there will be minimal or no effect on sorption of ^{237}Np due to Np-citrate complexes. Furthermore, tertiary complexes are thus not expected to form. This is sufficient evidence to reject working hypothesis (1) and (2). In absence of tertiary complexes, the drastic increase in sorption at high citrate concentrations is most likely due to ligand induced disturbances of the sediment which expose a greater number of surface sites for which ^{237}Np strongly binds; support of working hypothesis (3). The less drastic increase in K_d associated with the 50 mgC/L, 50 ppb ^{237}Np sample indicates that a limited number of excess sorption sites were exposed as a result of the ligand promoted dissolution of the sediment.

3.7.2. *Neptunium and Oxalate*

The strong complexation affinity between ^{237}Np and oxalate accompanied with the (approximately two fold) increase in experimental K_d values indicate that working hypothesis (2) is supported for the oxalate system. At low oxalate concentrations, as the oxalate complexes with the ^{237}Np , the majority of the Np-oxalate complex remains in the aqueous phase, as indicated by the lack of K_d increase at low and medium oxalate concentrations. Since the sorption affinity to the soil for ^{237}Np is already low and a further decrease in sorption was not observed, the Np-oxalate complex is not considered more favorable than the ^{237}Np sorption reaction for the fraction that has already sorbed. Thus, working hypothesis (1) is not supported. However, as the oxalate concentration is increased further, to 50 mgC/L, a larger fraction of the

^{237}Np exists as Np-oxalate complex as shown in the Geochemist Workbench models of section 3.1 (see Figure 1(a)). Hence, it becomes favorable under these conditions for a ternary, S-oxalate-Np, complex to form and noticeably increase the sorption of ^{237}Np . Thus, evidence for support of working hypothesis (2). Oxalate is not expected to have as drastic an effect on the soil surfaces as citrate, thus working hypothesis (3) is not considered to be a majority factor leading to the increased sorption observed in the oxalate system.

3.7.3. Neptunium, Citrate and Oxalate

The presence of both citrate and oxalate produced intriguing results that support multiple working hypothesis. Based on the citrate/oxalate results, comparison to the single ligand systems, Geochemist Workbench models supporting Np-oxalate complexation (and thus, S-oxalate-Np formation) as well as the citrate promoted dissolution of the soil, it appears that all working hypothesis are supported for this system. Comparing the citrate/oxalate system to the citrate system, the maximum K_d values decrease by about a third, supporting working hypothesis (1). This is thought to be due to the Np-oxalate complex forming, limiting sorption of ^{237}Np to the soil to some degree over the citrate system. As the citrate is still present and there is still a drastic increase in sorption in comparison to baseline results it is concluded that citrate induced disturbances of the soil still occurs thus, working hypothesis (3) is supported. In essence, the increase in sorption sites created by citrate dissolution of the soil increases sorption, as was done in the citrate system but, the presence of oxalate and the favorability of the Np-oxalate complex over the Np-S sorption reaction hinders this increase. It is also likely that some fraction of the Np-oxalate form Np-oxalate-S ternary complexes as proposed in the oxalate system, support of working hypothesis (2), but this is less obvious and judging by the only two fold K_d increase in the oxalate system it is a minor effect in comparison to the citrate dissolution of the soil.

3.8. Uranium

Geochemist Workbench models presented in section 3.1 show that greater than 99% of the aqueous uranium is complexed with either citrate or oxalate when the ligands are present, i.e. there is almost no free uranium in solution when these ligands are available. Thus, the ligands strongly bind uranium and as the ratio of ligand to uranium increases a coincident decrease in sorption of uranium would be expected. For example, citrate and other ligands have been shown to cause desorption and solubilization and thus, mobilize uranium (Kantar and Honeyman, 2006; Lozano et al., 2011; Read et al., 1998). Overall, from the baseline conditions to the systems with 50 mgC/L, this decrease in uranium sorption is experimentally confirmed and is most apparent in the 50 mgC/L samples at the highest ligand to uranium ratios (i.e. the 0.5 ppb and 5 ppb samples with 50 mgC/L) (Figure 7). The K_d values of the 50 ppb uranium with 50 mgC/L of citrate or oxalate are also lower than the baseline, but to a lesser degree, specifically by 917 mL/g and 543 mL/g respectively (Figure 7(a) and (b)). There is a more drastic decrease in K_d for the citrate/

oxalate combination to ~ 3 mL/g for the 50 ppb uranium sample, the lowest positive K_d attained (Figure 7(c)). The three order of magnitude decreases in K_d value observed at 50 mgC/L of the combined citrate and oxalate with 50 ppb uranium may be due to the alteration of the soil by citrate with further complexation by oxalate. The K_d values for samples containing 0.5 and 5 ppb uranium are negative for all 50 mgC/L samples (Figure 7), indicating that not only are the ligands preventing adsorption but they are also leaching native uranium from the soil. The distribution of uranium in this soil is unknown but is expected to be heterogeneous. Thus, the observed scatter in the data could be due to variations in the availability of native uranium in the soil. There are several outliers of this general decreasing trend within the data set for which no explanation has been determined as of yet; specifically, the slight increase in K_d values over baseline for several of the 0.5 and 5 mgC/L samples (Figure 7). In general, the minimized sorption at high ligand concentrations indicates that the citrate and/or oxalate L-M complexes are more favorable for uranium than is sorption to the soil. Thus, eliciting a decrease in sorption as the L-M complexes are formed and stay in solution, supporting working hypothesis (1).

(a)

(b)

(c)

Figure 7: Distribution coefficients for UO_2^{2+} with SRS soil at baseline conditions (0 $\text{mg}_\text{C}/\text{L}$) and in the presence of varying concentrations (0.5, 5, and 50 $\text{mg}_\text{C}/\text{L}$) of (a) citrate, (b) oxalate and (c) citrate/oxalate mixture. The citrate/oxalate mixture samples contain 0.5, 5 or 50 $\text{mg}_\text{C}/\text{L}$ of each ligand.

Working hypothesis (2) and (3) do not appear to be supported in the uranium system. The rejection of these working hypothesis is based on the noted decrease in K_d values with increasing ligand concentration. With regards to working hypothesis (2), this decrease indicates that the ligands are not forming ternary complexes with uranium and the soil surfaces. If such a complex were forming an increase in K_d values would be observed with increasing ligand concentration. Furthermore, the rejection of working hypothesis (3) is corroborated since there was not an increase in K_d values for the highest citrate and/or oxalate concentrations as was observed for ^{99}Tc and ^{237}Np . Thus, it is evident that the L-U complexes appear to remain in the aqueous phase even if the surface coatings of the soil are disturbed as discussed above.

4. Conclusion

Amendment of batch sorption studies on SRS soil with citrate and/or oxalate increased the sorption of ^{99}Tc and ^{237}Np over baseline results for the highest ligand concentrations, had little to no effect on ^{133}Cs sorption, and decreased sorption of U (even causing dissolution of native uranium). The primary mechanism for the increased sorption of ^{99}Tc is hypothesized to be due to ligand facilitated dissolution of the clay fraction of the soil. This also is thought to play a role in the increased sorption of ^{237}Np combined with formation of Np-oxalate and thus, S-oxalate-Np complexes. The decreased sorption and dissolution of U is attributed to the favorability of ligand-U aqueous complexes over sorption to the soil. The alteration of the mobility and sorption behavior of ^{99}Tc , ^{237}Np and U in the organic ligand amended systems of this work indicates that if these ligands are present in the contaminated subsurface, the *in-situ* biogeochemistry of these nuclides has the potential to be altered.

The variability in the exhibited sorption behavior as a result of citrate and oxalate amendments is a result of the wide range of biogeochemistry of this suite of nuclides owing to the inherent properties, interaction mechanisms and behavior of each particular type of ion. While these results were not entirely unexpected, they do provide valuable insight into the systems particular to SRS. Thus, these studies are seen as

stepping stones and the results herein will be used to guide future work in elucidating the potential impacts that plant exudates may have on the biogeochemical behavior of this suite of nuclides.

Additionally, the numerical K_d values and trends determined in these studies as well as the general effects of the ligands (particularly citrate) on the soil can be used to directly inform increasingly complicated miscible displacement studies and modeling efforts for the larger overarching research initiative at hand. As shown in Table 2, the K_d values measured in this work in the absence of organic ligands are comparable to several previous studies on soils with similar properties to the sandy clay loam used in this work. The variation in K_d values in the presence of citrate and oxalate indicates a potential change in the mobility of the ion based on the change in chemical speciation or a change in the ligand-mineral or ligand-ion interactions. Moreover, previous studies have examined sorption of the individual ions of interest in this paper to soils. However, using one soil in this work to examine multiple radionuclides will allow for a self-consistent comparison of the data for which can aid in the testing and validation of thermodynamic sorption databases. This will be the subject of future work regarding these soil-radionuclide systems.

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