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^{129}I, ^{99}Tc, and U Distribution Coefficients of Subsurface Sediments Collected from the Proposed Site of the Environmental Management Disposal Facility

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EXECUTIVE SUMMARY

Performance Assessment calculations were completed in 2020 to evaluate the Environmental Management Disposal Facility (EMDF), a proposed new low-level radioactive waste (LLW) disposal facility on the U.S. Department of Energy's Oak Ridge Reservation (ORR). Among the large number of input parameters needed for such calculations, are distribution coefficients (K_d values; radionuclide concentration solid:liquid ratio) that provide a measure of the tendency of radionuclides to bind to sediments. The objective of this study was to measure K_d values of three radionuclides that may pose a disproportionately large amount of risk, U, ^{129}I and ^{99}Tc. The average I K_d value for the 14 geological materials recovered from the proposed EMDF site was 37.8 mL/g and ranged from -1.8 to 140.9 mL/g. These values were consistent, but somewhat larger than previous measurements made with ORR sediments and were about an order of magnitude greater than those used in previous EMDF PA calculations. The median Tc K_d value was 365.7 mL/g, much greater than previously reported using ORR geological materials. Five of the 14 tested geological materials sorbed large quantities of Tc, suggesting that the weakly sorbing Tc(VII) species had been reduced to the sparingly soluble Tc(IV) species. The five strongly sorbing sediments had apparent Tc solubility values of approximately $<10^{-8}$ mol/L. The median U K_d value was 5,726 mL/g. All of the tested geological materials had large K_d values, ranging from 625 to >10,208 mL/g. Among the sediment samples that exhibited strong U binding, the apparent solubility value was approximately $<10^{-9}$ mol/L. Based on sediment properties and general ORR geological considerations, it was proposed that much of the I and Tc retention could be attributed to the site materials exhibiting low pH (average pH = 4.94), low redox status, and/or the elevated levels of iron oxides, manganese oxides, and natural organic matter. Similarly, the extremely high U binding measured in these sediments may also be attributed to the low conditions of carbonates, which can complex and therefore solubilize uranyl in these tests due to the low pH, and also the relatively high concentrations of iron and organic coatings on these samples. An implication of this study is that the areas of the EMDF subsurface environment may have natural properties for attenuating I, Tc, and U movement, and potentially other radionuclides, thereby possibly reducing risk posed by burial of LLW at this site.

This document is a revision of SRNL-STI-2021-00404, Revision 0 that includes new data describing U K_d values and new I and Tc K_d values for four Nolichucky sediments. These new results were integrated into the data presented in the original document.

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LIST OF ABBREVIATIONS

ANOVA	analysis of variance
d.f.	degrees of freedom
EMDF	Environmental Management Disposal Facility
I	iodine
K_d	distribution coefficient
LLW	low-level waste
OM-LOI	organic matter – loss on ignition
ORP	oxidation-reduction potential
ORNL	Oak Ridge National Laboratory
ORR	Oak Ridge Reserve
p	probability
SRNL	Savannah River National Laboratory
SWSA	Solid Waste Storage Area
Tc	technetium
U	uranium
ZPC	Zero-point of charge

1.0 Introduction

The Environmental Management Disposal Facility (EMDF) is a proposed low-level waste (LLW) disposal facility located on the Oak Ridge Reservation (ORR), Oak Ridge, TN. A performance assessment (PA) of the EMDF has been completed that provides, amongst other information, an estimate of the long-term health risk posed by the proposed facility (UCOR, 2020). It includes site-specific model simulations for release of radionuclides from the disposal facility, dose analyses for post-closure exposure to releases, and analysis of inadvertent human intrusion scenarios. These calculations required a large number of site-specific input parameters, including geochemistry parameters, to estimate the tendency for radionuclides to interact with the surrounding sediment. Two types of geochemical input parameters that are commonly used in PAs are the distribution coefficient (K_d), which is the radionuclide concentration solid:liquid ratio, and the apparent solubility value (k_s), the radionuclide aqueous concentration in the presence of a radionuclide-containing solid phase. In an effort not to underestimate the potential risk posed by disposing of LLW in the subsurface, PA models often include conservative assumptions. In the case of geochemistry parameters, such conservative assumptions would include lower K_d and higher k_s values than actually expected, thereby maximizing the estimate of radionuclide concentration in the mobile aqueous phase that may adversely affect human health.

1.1 Objectives

Among the radionuclides anticipated to pose high levels of risk at the EMDF are ^{129}I, ^{99}Tc and U. The objective of this study was to measure ^{129}I, ^{99}Tc, and U K_d values of 14 subsurface sediments collected from the location of the proposed EMDF. The intent of this work was to improve the accuracy of input values used in future PA calculations and to reduce uncertainty and unnecessary conservatism introduced through the use of literature-derived K_d values as opposed to site-specific K_d values. Including unnecessary conservatism in PA models may result in unnecessarily high disposal costs.

2.0 Experimental Procedure

2.1 Sediment and groundwater samples

Fourteen geological samples and one groundwater sample were collected by ORR personnel (Table 2-1). Sampling locations were based on the types of materials which LLW radionuclides at the EMDF may contact. Geological samples selected include geological materials that may be used as clean fill in the waste cell and/or as low-permeability materials for the liner system, geological buffer layer, structural fill, and geological materials that represent the in-situ materials below the geobuffer. The EMDF facility design requires removal of >3 m of existing geological material prior to construction, and therefore deeper geological materials may be exposed to the plume path and need to be studied. Therefore, the fourteen geological samples included three sediments and three saprolite samples from the Maryville formation, four sediments from the Chestnut Ridge formation, and three weathered sediment and one saprolite sample from the Nolichucky formation (Table 2-1).

The Maryville and Chestnut Ridge samples were collected from two borrow areas located near the proposed EMDF facility. The Site 7b borrow area is located on the Maryville limestone and the Chestnut Ridge borrow area is located on the Knox limestone group. The Nolichucky samples were collected along Haul Road and Bear Creek Road (details are provided in the Appendix Table 2-6). About 2 kg of each sample was collected, double bagged in zip-lock bags, and then shipped to the Savannah River National Laboratory. The Maryville and Chestnut Ridge samples were sent in April 2019, and the Nolichucky samples were sent in March 2022. A conscious effort was made to minimize changes during storage to the field redox status of the geological samples by placing them in the dark and in a 5 °C refrigerator prior to using in the sorption experiments. Within a week of receiving the 2-kg samples, the samples were extensively mixed in the zip-lock bags, and then 0.1 kg subsamples were retrieved from multiple locations within the 2-kg well-mixed sample for later use in the sorption experiments as described in section 2.2.

Table 2-1. Sediment sample descriptions.

Field Sample ID#	Field Sampling Date	Formation	Geological Material	Top Depth of Sediment Core (ft)	Bottom Depth Sediment Core (ft)
ETP32-KD-6.5	4/16/2019	Maryville	Sediment	6.5	7.5
ETP35-KD-8	4/15/2019	Maryville	Sediment	8	9
ETP27-KD-8.5	4/24/2019	Maryville	Sediment	8.5	9.5
EBH42-KD-20	4/16/2019	Maryville	Saprolite	20	25
EBH43-KD-20	4/15/2019	Maryville	Saprolite	20	25
EBH44-KD-20	4/17/2019	Maryville	Saprolite	20	25
ETP51-KD-3	4/17/2019	Chestnut Ridge	Sediment	3	4
ETP43-KD-5	4/18/2019	Chestnut Ridge	Sediment	5	6
ETP48-KD-6	4/23/2019	Chestnut Ridge	Sediment	6	7
ETP49-KD-9	4/23/2019	Chestnut Ridge	Sediment	9	10
HR-EMDF-1	3/4/2022	Nolichucky	Sediment	3	4
HR-EMDF-2	3/4/2022	Nolichucky	Sediment	3	4
BCR-EMDF-1	3/4/2022	Nolichucky	Saprolite	5	NA
BCR-EMDF-2	3/4/2022	Nolichucky	Sediment	5	NA

A 2-L uncontaminated groundwater sample was collected from Project Environmental Measurements System Monitoring location GW-989. This well is located near the proposed EMDF and is expected to be representative of the water that may receive radionuclides leached from the disposed waste. The well was purged with the equivalent of one height-of-water-column prior to collecting the sample. Some water chemistries are presented in Table 2-2. The groundwater sample was shipped together with the sediment samples and stored until used in a light-excluding box in a 5 ^{o}C refrigerator. A second groundwater sample was collected in 2022 from the same well. Chemical characterization can be found in Appendix Table 5-8 of this second sample, and is similar to data reported in Table 2-2.

Table 2-2. Groundwater (GW-989) chemical properties.

Property (unit)	**Value**	**Measurement [a]**
Conductivity (µS/cm; ± 10%)	390	Field Measurement[b]
Dissolved Oxygen (ppm; ± 10%)	1.95	Field Measurement
Temperature (°C; (±1.0 °C)	16.2	Field Measurement
pH (± 0.1 units)	6.99	Field Measurement
ORP (mV; ± 10%)	133	Field Measurement
Turbidity (NTU)	>1000	Field Measurement
Nitrate (µg/L)	171	Lab Measurement: EPA-300.0
Chloride (µg/L)	1650	Lab Measurement: EPA-300.0
Sulfate (µg/L)	19200	Lab Measurement: EPA-300.0
Bicarbonate (µg/L)	200000	Lab Measurement: EPA-310.1
Carbonate (µg/L)	4000	Lab Measurement: EPA-310.1
Dissolved Solids (µg/L)	253000	Lab Measurement: SM-2540 C
Dissolved Organic Carbon (µg/L)	890	Lab Measurement: SM-5310 B
Magnesium (µg/L)	10100	Lab Measurement: EPA SW846-6010C
Sodium (µg/L)	10300	Lab Measurement: EPA SW846-6010C
Aluminum (µg/L)	200	Lab Measurement: EPA SW846-6010C
Potassium (µg/L)	1260	Lab Measurement: EPA SW846-6010C
Calcium (µg/L)	69000	Lab Measurement: EPA SW846-6010C
Iron (µg/L)	100	Lab Measurement: EPA SW846-6010C

[a] Lab measurements were conducted at GEL Laboratories, LLC, Charleston, SC by the standard methods noted (APHA, 2005; EPA, 2019a, b).
[b] Field measurements were taken at the time of groundwater sample collection by ORR field staff.

2.2 Distribution Coefficient, K_d Value, Measurements

Laboratory batch sorption tests were conducted following the standard test method ASTM C1733-10 (ASTM, 2010). Briefly, the geological samples were air-dried at room temperature overnight until there was no weight change due to water evaporation and then passed through a 2mm sieve (>95% of the sample passed through the 2mm sieve). About 1.000 ± 0.005 g of air-dried geological material was combined with 24.900 ± 0.005 g of groundwater in a 45-mL centrifuge tube. The exact mass of geological material and groundwater were recorded for each sample. The suspension pH of each tube was measured. The suspensions were then amended with 0.1 mL of either 6.67 Bq/mL^{129}I (as I^-), 1050 Bq/mL ^{99}Tc (as TcO_4^-), or 1000 ppb U (as UO_2^{2+}). These working solutions were made by diluting with deionized water 74,000 Bq/mL standard solutions of ^{129}I (Eckert & Ziegler) and ^{99}Tc (Eckert & Ziegler, Atlanta). The U spike was taken directly from a 1000 ppb U standard solution used for ICP-MS calibrations (Calibre Scientific Ltd.). Following this protocol (ASTM, 2010), the selected radionuclide amendment concentrations were based on the suggestion of using as a low concentration as possible that would provide a measurable K_d value. As will be described in the results section, the concentration of ^{129}I and U amendments were appropriate, whereas a greater ^{99}Tc amendment was warranted for some of the tested sediments.

The samples were then put on a slow-moving platform shaker at room temperature for two weeks. After equilibration, the samples were taken off the shaker, permitted to settle for about 10 minutes, and then 10 mL was removed from each suspension and passed through a 0.45 µm filter. The filtered samples were then analyzed for ^{129}I, ^{99}Tc, or U as described in Section 2.3.1. Each K_d measurement was duplicated, and a no-sediment control was included to provide information about the final radionuclide amendment concentration and whether radionuclides were sorbed (lost) to labware. There was no loss of either ^{129}I, ^{99}Tc, or U to labware. The experimental design was:

(14 geological materials × 2 reps × 3 radionuclides) + (1 no-sediment control × 3 reps × 3 radionuclides) = 93 treatments.

The K_d values were calculated using Equation 1:

$$K_d = \frac{(C_0 - C_{eq}) \times V_{aq}}{C_{eq} \times M_{sed}} \tag{1}$$

where C_0 and C_{eq} are the radionuclide concentrations of the aqueous phase at time 0 and at the end of the 2-week equilibration period, respectively. V_{aq} is the aqueous volume and M_{sed} is the mass of the geological materials used in the K_d batch suspension.

2.3 Analytical Methods

2.3.1 Analytical Methods

^{129}I and ^{99}Tc concentration measurements for the K_d tests were conducted by the Savannah River National Laboratory's Analytical Methods group following standard methods (EPA, 1998). Briefly, ^{129}I was analyzed using a shielded low-energy high purity germanium (HPGe) gamma ray spectrometer for periods ranging up to 800 minutes. This resulted in detection limits as low as ~30 dpm/L (80 parts per trillion). ^{99}Tc samples were analyzed using liquid scintillation counting for 10 – 600 minutes and had detection limits of ~0.4 dpm/mL (~11 parts per trillion). Uranium was detected using an ICP-MS (7850 ICP-MS Agilent). The detection limit was 0.1 ppb.

2.3.2 Sediment Characterization Methods

The 14 sediments were analyzed for pH, loss-on-ignition (360 ºC), total sand, and silt + clay using standard methods (Sparks, 1996). These analyses were conducted in duplicate and with subsamples from the air-dried, <2mm, sample used for the K_d testing. Briefly, pH was measured in a 2:1 water:sediment suspension after the suspension had equilibrated for at least 30 min.

Loss-on-ignition estimates soil organic matter based on gravimetric weight change associated with high temperature oxidation of organic matter (Schulte and Hopkins, 1996). After initial oven drying at 105ºC to drive off water, the sediment samples were placed in a muffle furnace for 2 hours at 360ºC. The percent weight loss during the ignition step was reported as OM-LOI (wt-% loss) with a method detection limit of 0.05 wt-%. This method has been reported to overestimate OM concentrations in sediments rich in gypsum and other carbonate phases, but because all 14 sediments were quite acid, ranging in pH from 4.63 to 5.52, only negligible amounts of gypsum or carbonate phases were expected to be present. The low pH values and the assumption that there were low carbonate phases present in these materials are supported by earlier mineralogy analyses of geological materials collected from this area (Driese et al., 2001; Jardine et al., 1993).

Sieve analysis was conducted using two sieves, 2 mm (ASTM #10 sieve) and 0.053 mm (ASTM #270 sieve) and assigned particle size classes were adopted from the Soil Science Society of America (Sparks, 1996). About 50 g of <2 mm air-dried sediment was passed through a 0.053 mm sieve. The fraction retained was defined as the sand fraction and the fraction that passed through the 0.053 mm fraction was defined as the "silt+clay" fraction. According to the Soil Science Society of America, silt size particles are <0.050 and >0.002 mm, and clay size particles are <0.002 mm.

3.0 Results and Discussion

3.1 Iodine K_d Values

3.1.1 Iodine K_d Value Results

Measured I K_d values and various sediment and saprolite properties are presented in Table 3-1 and the descriptive statistics of these parameters are presented in Table 3-2. The 14 I K_d values (each measured in duplicate) ranged from -1.8 to 140.9 mL/g and had a mean of 37.8 ± 11.2 mL/g (Table 3-2). The negative K_d value can be attributed to data noise and is not physically real. The 14 geological materials had remarkably uniform pH values of 4.89 ± 0.07 with a range of 4.60 to 5.52 and uniform OM-LOI of 0.15 ± 0.01 wt% with a range of 0.11 to 0.22 wt-%. The particle size distribution of the three formations were also similar, on average 88 wt% sand and 12 wt% silt+clay. The Duncan's Multiple Range Test indicated that there was a significant ($p \geq 0.05$) difference between the mean I K_d values for the three sediments, such that Chestnut Ridge > Maryville > Nolichucky (Table 3-3). There were no significant differences between the weathered sediment and the saprolite samples in the Maryville formation (Table 3-3). It was not possible to conduct similar comparisons with the other two formations because no saprolite was collected from the Chestnut Ridge formation and only one saprolite sample was collected from the Nolichucky formation.

3.1.2 Iodine K_d Values Compared to Previously Reported Values

These I K_d values are comparable to previously measured I K_d values that used soils and saprolite of the Maryville formation (Davis et al., 1984; Rothschild et al., 1994). Rothschild et al. (1994) measured I K_d from soil collected from the Solid Waste Storage Area 7 site and nearby stream water spiked with ^{125}I. The soils were generally collected from shallower depths (<0.5 m) than those from this study. The K_d values and associated geochemical parameters from Rothschild et al. (1994) are presented in Appendix Table 5-1, where the 15 I K_d values had an average of 17.1 ± 13.4 mL/g and a range of 3.6 to 54.4 mL/g. The equilibrium pH values were quite similar to those in this study (Table 3-2); they ranged from 4.6 to 6.2. The average OM concentration reported by Rothschild et al. (1994) (Appendix Table 5-1) was 3.31 ± 1.2 wt-%, which is greater than those measured in this study. This difference may be due to the fact that Rothschild et al. (1994) collected several shallow samples (<0.5m) that they referred to as 'soils", which by definition includes the root zone. Also, they used a wet-chemistry method rather than the loss-on-ignition analytical method to measure OM.

Davis et al. (1984) reported I K_d values for soil and saprolite materials that are similar to those expected at the EMDF. They collected Conasauga group soils from Solid Waste Storage Area 6, for measurements intended to be relevant to the LLW disposal site, shallow land burial. They collected three profiles between a depth of 0.2 to 2 m from three trenches. Their average I K_d value was 11.7 ± 9.0 mL/g with a range of 1 to 21.4 mL/g (summarized in Appendix Table 5-2). They reported similar acidic pH values 4.4 ± 0.3 as reported here in Table 3-2 and as reported by Rothschild et al. (1994). They reported OM concentrations of 0.37 ± 0.41 wt% that ranged from 0.12 to 1.4 wt%, which is greater than those reported here in Table 3-2. Again, the lower average OM concentrations may in part be attributed to the fact that some geological materials used in this study were originated from greater depths.

3.1.3 Discussion of potential geochemical processes responsible for iodine sorption

The combination of pH, OM, iron- and manganese-oxide, and mineralogical conditions that exist at the EMDF site in Bear Creek would be expected to promote the sorption of iodine. Conversely, geochemical conditions known to diminish iodine binding are less likely to exist at the site, including low OM (<0.1 wt%), low iron- and manganese-oxide content substrates, and high pH values (pH >~8). Davis et al. (1984) and Rothschild et al. (1994) attributed the appreciable iodine uptake by the geological materials they studied to the low pH conditions and the relatively high abundance of iron and manganese oxides and natural OM.

Organic matter: Organic content of the soil is a key soil parameter influencing iodine sorption (EPA, 2004; Kaplan et al., 2014). Iodine can form very strong bonds with soil organic matter (covalent bonds) and slight increases in OM concentrations, even at trace levels (0.1 to 0.4 wt%), can result in corresponding increases in I K_d values (Kaplan et al., 2014; Xu et al., 2015). Furthermore, OM may bind I via electrostatic complexation processes, which are pH dependent (described in more detail below).

pH, iron oxide, manganese oxide, and organic matter interactions: As a general rule, lower pH, greater iron and manganese oxide contents, and greater OM contents result in greater I sorption (EPA, 2004; Kaplan et al., 2014). At low pH values, mineral surfaces and OM become protonated and have a net positive charge, whereas at higher pH values, the surfaces become deprotonated and have a net negative charge. Iron and manganese oxides and OM have pH-dependent charge, which promotes greater anion exchange capacity at lower pH levels. The critical pH delineating net positive and net negative charge of a mineral is referred to as the zero-point-of-charge (ZPC) (Cristiano et al., 2011). For example, the ZPC for goethite (α-FeOOH) is about pH 7.5 and pyrolusite (β-MnO_2) is about pH 5.9 (Cristiano et al., 2011). The ZPC of OM varies greatly depending on its source, age, and how it is measured, but is commonly measured between pH 6 and 8 (Stumm and Morgan, 2012).

Goethite is the most common iron oxide and pyrolusite is the most common manganese oxide in the soil environment, and both of these oxides are highly chemically reactive (Dixon and Weed, 1989). At the pH of the EMDF (pH 4.94; Table 3-2), both of these minerals would be expected to have a net positive charge, thereby they would electrostatically attract anions, including iodide (I^-), iodate (IO_3^-), and pertechnetate (TcO_4^-). The iron and manganese oxide contents in Conasauga soils, saprolite, and shale bedrock are considered high. For example, Rothschild et al. (1984; as shown in Appendix Table 5-1) reported relatively high sediment manganese concentrations of 412 ± 322 mg/kg and sediment iron concentrations of 139 ± 69 mg/kg (Rothschild et al., 1994).

Table 3-1. Sediment and Saprolite I, Tc, and U K_d and apparent solubility values, and geological properties (average of duplicate or triplicate measurements).

ORR Sample ID	SRNL Sample ID	Formation	Weathered Sediment or Saprolite	Sample depth	I K_d	Tc K_d	Apparent Tc solubility[a]	U K_d	Apparent U solubility[a]	pH	OM-LOI	Sand	Clay+Silt
				(m)	(mL/g)	(mL/g)	(mol/L)	(mL/g)	(mol/L)	(unitless)	(wt-%)	(wt-%)	(wt-%)
ETP32-KD-6.5	805	Maryville	Sediment	2.0–2.3	56.0	>1320.0	<7.5E-08	>9135	<4.7E-10	4.63	0.11	87.1	12.9
ETP35-KD-8	806	Maryville	Sediment	2.4–2.7	46.3	7.5	NA	>7212	<7.1E-10	4.65	0.15	84.9	15.1
ETP27-KD-8.5	803	Maryville	Sediment	2.6–2.9	21.3	>2628.3	<2.2E-09	7854	5.4E-10	4.90	0.15	85.1	14.9
EBH42-KD-20	809	Maryville	Saprolite	6.1–7.6	44.2	375.6	NA	1922	NA	4.88	0.14	84.8	15.2
EBH44-KD-20	802	Maryville	Saprolite	6.1–7.6	5.9	>1831.9	<3.9E-09	622	NA	4.82	0.11	91.2	8.8
EBH43-KD-20	804	Maryville	Saprolite	6.1–7.6	2.7	355.8	NA	1484	NA	4.77	0.12	85.5	14.5
ETP51-KD-3	807	Chestnut Ridge	Sediment	0.9–1.2	92.7	>1317.6	<9.3E-08	3831	1.1E-09	4.82	0.17	91.6	8.4
ETP43-KD-5	801	Chestnut Ridge	Sediment	1.5–1.8	140.9	1.5	NA	3961	1.1E-09	5.52	0.15	76.6	23.4
ETP48-KD-6	810	Chestnut Ridge	Sediment	1.8–2.1	65.4	467.2	NA	3957	1.1E-09	5.28	0.12	92.1	7.9
ETP49-KD-9	808	Chestnut Ridge	Sediment	2.7–3.0	47.8	1147.1	5.1E-09	>10165	<4.2E-10	5.18	0.17	91.1	8.9
HR-EMDF-1	811	Nolichucky	Sediment	1.0-1.2	1.0	0.12	NA	6026	7.1E-10	4.75	0.15	89.9	10.1
HR-EMDF-2	812	Nolichucky	Sediment	1.0-1.2	-1.8	1.06	NA	5425	7.9E-10	4.58	0.17	90.6	9.4
BCR-EMDF-1	813	Nolichucky	Saprolite	1.5	4.4	2.14	NA	>7436	<6.7E-10	4.96	0.22	90.6	9.4
BCR-EMDF-2	814	Nolichucky	Sediment	1.5	2.3	-0.51	NA	>8272	<5.5E-10	4.69	0.13	90.5	9.5

[a] Apparent solubility values were calculated for only those samples that demonstrated extraordinary high Tc or U uptake, suggestive that precipitation rather than adsorption/exchange was controlling uptake. All other values were assigned “NA” (not applicable).

Table 3-2. Descriptive statistics of sediment and saprolite properties and I, Tc, and U K_d values.

	I K_d	Tc K_d [a]	U K_d [a]	pH	OM-LOI	Sand	Clay+Silt
	(mL/g)	(mL/g)	(mL/g)		(wt-%)	(wt-%)	(wt-%)
Mean	37.8	NA	NA	4.89	0.15	64.9	35.1
Standard Error	11.2	NA	NA	0.07	0.01	9.8	9.8
Median	32.8	365.7	5726	4.82	0.15	85.0	15.0
Standard Deviation	41.9	NA	NA	0.27	0.03	36.5	36.5
Minimum	-1.8	-0.5	622	4.60	0.11	9.4	7.9
Maximum	140.9	2628	10165	5.52	0.22	92.1	90.6
Count	14	14	14	14	14	14	14

[a] Few descriptive statistics were available for Tc and U K_d values because of the presence of greater-than values (Table 3-1).

Table 3-3. Mean K_d values and geological property values of formations.

Formation	Weathered Sediment or Saprolite	Number of observations	I K_d [a]	Tc K_d [b]	U K_d [b]	pH	OM- LOI	Sand	Clay+Silt
Maryville	All samples	6	29.4 B	>1086.5	>4567	4.77 B	0.13	86.4	13.6
Chestnut Ridge	All samples	4	86.7 A	>733.3	3959	5.20A	0.15	87.9	12.1
Nolichucky	All samples	4	1.5 C	0.7	>6731	4.75 B	0.17	90.4	9.6

[a] Capital letters within a column indicate significant differences according to Duncan's Multiple Range Tests ($p \leq 0.05$). No statistical tests were conducted on Tc K_d and U K_d data because of the presence of greater-than-values.

[b] Median values

Following the conceptual geochemical model put forth by Watson et al. (2004) for the Oak Ridge Field Research Center located in Bear Creek, the pH in the soil/saprolite above the water table is expected to be acidic, pH 4.5 to 6.0, while the pH in the aquifer will be near neutral, 7 to 8. Therefore, pH conditions in the soil/saprolite of the vadose zone may be especially well suited for binding I.

Illite: In an evaluation of various soil minerals (as opposed to quarried minerals), illite, a common mineral at the ORR and within the Conasauga soil profiles, had the greatest iodine K_d value, 15.14 mL/g (Kaplan et al., 2000), of the wide suite of investigated minerals. Mineralogical characterization of soils (Davis et al. (1984) page 58, Table 17) and bedrock (Davis et al. (1984), page 22, Table 3) of the Maryville limestone indicates illite to be the predominant clay mineral. Rothschild et al. (1994) also found illite to be abundant in the clay size fraction of Conasauga group soils at ORNL ((Rothschild et al., 1994), pages 53-60). Similarly, mineralogical analysis of the Nolichucky shale (Meyer et al. (1987), page 4, Table 3.1) identified illite to be the most abundant of all minerals including quartz and feldspars. Significant I sorption to illite over a very wide range of pH values has been demonstrated (Kaplan et al., 2000). Iodide K_d values increased from 22 to 46 mL/g as the pH of an illite suspension decreased from 9.4 to 3.6 (Kaplan et al., 2000). At a pH of 5.0, the approximately pH measured in the samples from this study, Kaplan et al. (2000) reported that illite had an iodide K_d of 59 ± 2.2 mL/g).

3.2 Technetium K_d Values

3.2.1 Technetium K_d Value Results

Tc K_d values and various sediment and saprolite properties are presented in Table 3-1 and the descriptive statistics of these parameters are presented in Table 3-2. The 14 Tc K_d values ranged from -0.5 to >2628.3 mL/g and had a median of 365.7 mL/g (Table 3-2). The negative K_d value can be attributed to data noise and is not physically real. Four of the sediments, three from the Maryville and one from the Chestnut Ridge formation, sorbed extremely large amounts of Tc, resulting in K_d values that were too high to quantify. This geochemical behavior of high Tc sorption is strongly suggestive that the added TcO_4^-, the weakly binding form of Tc, had undergone chemical reduction to Tc^{4+}, a sparingly soluble and strongly binding form of Tc. The batch sorption tests conducted for this study cannot distinguish between adsorption/exchange processes and coprecipitation/precipitation processes. However, this distinction is important for PA calculations because the two binding processes result in differences in how the model partitions Tc between the solid and liquid phases. The K_d construct describes a fixed concentration ratio between the two phases, while the apparently solubility construct, k_s, describes a fixed aqueous concentration based on the solid phases controlling solubility, but does not control Tc concentrations in the solid phase. Tc K_d values >1000 mL/g were also expressed as apparent solubility values in Table 3-1. Four out of the five apparent solubility values were below detection limits, generally <9.3×10^{-8} mol/L, however a weathered sediment from the Chestnut Ridge formation (sample ETP49-KD-9) had a measurable apparent solubility value of 5.1×10^{-9} mol/L (Table 3-1). To put this value into thermodynamic context, the approximate solubility of crystalline $TcO_{2(cry)}$ is ~10^{-9} mol/L and is ~10^{-8} mol/L for more amorphous forms of $TcO_{2(am)}$ and $TcO_2\text{-}x H_2O$ (Meyer et al., 1991; Pearce et al., 2018).

3.2.2 Technetium K_d Values Compared to Previously Reported Values

Two studies were identified that measured Tc K_d values using geological materials potentially representative of those in the EMDF subsurface (DOE-OR, 1992; Meyer et al., 1987). DOE-OR (1992) reported K_d measurements of Tc (along with Cs, Sr, Np, and U) using various soils recovered from Bethel Valley near the Waste Area Group 1. They obtained an average Tc K_d value of 0.72 ± 0.16 mL/g with a range of 0.53 to 1.04 mL/g (see Appendix Table 5-4). Noteworthy, they reported that Tc had no time dependency of sorption, suggesting that steady state conditions with respect to Tc were achieved in ≤1 day. This has important implications because flow through fractured media in the EMDF subsurface may be faster than through porous media. This data indicates that the full extent of Tc sorption is completed in a relatively short period of time.

Meyer et al. (1987) measured Tc K_d of five shale samples using three types of simulated groundwater: a concentrated brine (3.42 mol/kg, pH 5), dilute brine (100/1 dilution of the concentrated brine), and a bicarbonate (0.03 mol/L) Appendix Table 5-5. Unfortunately, these studies were conducted under much greater pH conditions (average pH = 8.13) than existed in this study (average pH = 4.94). As will be discussed in greater detail in section 3.2.3, the elevated pH would be expected to decrease TcO_4^- sorption, and indirectly impact Tc oxidation state (assuming all other conditions are held constant, increases in pH would promote Tc oxidation). The Tc K_d values for the concentrated brine and dilute brine ranged from 0.3 to 266 mL/g Appendix Table 5-5. Of the shale samples evaluated by Meyer et al. (1987), the Nolichucky shale is most relevant to the EMDF PA. The K_d value for the dilute brine and bicarbonate groundwater were 12.2 ± 0.3 mL/g and 12.3 ± 0.3 mL/g, respectively. The K_d values in the Upper Dowelltown were as great as 266 mL/g, which appears to have been measured under partially reducing redox conditions.

In this study, Tc uptake varied greatly not only between samples, but also between replicates of the same sample (Appendix Table 5-3). The high variability between replicates may in part be attributed to the existence of varying redox microenvironments in the geological samples. The samples were very well mixed both prior to removing from the zip-lock sample bags as well as during the 2-mm dry-sieving process. However, the existence of reducing microenvironments, including those occurring within mm-sized soil aggregates, is well documented (Foster, 1988; Schlüter et al., 2018; Yang et al., 2020). Varying redox conditions would have an impact on measured Tc K_d values because the K_d value for Tc(IV) has been measured to be 4 to 5 orders of magnitude greater than that for Tc(VII) (Kaplan, 2021). In the conceptual model of the Oak Ridge Field Research Center located in Bear Creek Valley on the ORR, Watson et al. (2004) described the oxidation-reduction state of the system as primarily oxidizing, but with microenvironments of reducing conditions. These reducing microenvironments were identified using microbial genomics information. Future Tc K_d measurements warrant a greater number of replicates than was used in this study to account for the high redox variability of these materials. Two replicates were selected for this study based on the variability reported in DOE-OR (1992) and Meyer et al. (1987) and based on the practical consideration that the objective of this study was to test as many samples as possible for the available resources.

The conflicting results between those reported in DOE-OR (1992) and Meyer et al. (1987) and those reported in Table 3-1 may be attributed to intrinsic differences in the mineralogy of samples, sample handling and storage, and/or in the case of Meyer et al. (1987), differences in procedure where they adjusted the pH to be highly alkaline. Regarding sample handling and storage, some attempt was made to maintain field redox conditions, as described in the Materials and Methods section, section 2.2. No information about sample handling was provided in DOE-OR (1992) or Meyer et al. (1987), which suggests they may have followed routine procedures, which would not refrigerate or minimize contact with air.

Finally, the Tc K_d values measured in this study were much greater, especially for the Maryville and Knox formations, than the conservative values used in the 2020 PA of the EMDF: 0.36 mL/g for the Waste Zone, 0.72 mL/g for the Vadose and Saturated Zone, and 0.04 for the screening model (UCOR, 2020; Table 3.4). These results also suggest that there may be an opportunity for the EMDF PA to further reduce conservatism in the Tc K_d values by conducting future studies specifically designed to mimic subsurface environmental conditions. Building on the results from this and the previous studies, Tc sorption measurements could be improved by: 1) taking additional precautions during sampling and shipment to minimize the extent that geological material come in contact with air, 2) conducting the batch sorption tests with field moist sediment upon arrival from the field, 3) using greater initial concentrations of $^{99}TcO_4^-$ that would permit measuring Tc solubilities, perhaps down to 10^{-10} M, and 4) including more replicates to compensate for the intrinsic redox heterogeneity existing in these geological materials. Importantly, conducting the sorption in an inert glovebox may be helpful for providing end member measurements under reducing conditions but may not provide defensible conservative estimates representative of field conditions.

3.2.3 Discussion of potential geochemical processes responsible for technetium sorption in these experiments

The primary conditions influencing Tc geochemistry are Eh (or redox status), pH, and the presence or absence of iron oxides, manganese oxides, and natural OM (Icenhower et al., 2010). Each of these parameters are discussed here.

Redox status: Technetium exists in nature either as the highly mobile oxidized species, TcO_4^-, or the appreciably less mobile and less soluble Tc^{+4} species. As noted above in section 3.2.1, either very small or very large amounts of the added dissolved TcO_4^- were removed by the geological samples. These tests initially added TcO_4^- to the geological material suspensions, but there were no measurements to confirm the oxidation state after contact with the geological materials. The sorption data in Table 3-1 suggests, but is not proof, that both species were likely present, depending on the solids in the system.

Organic matter: Due to the large number of pH-dependent exchange sites in OM, and the fact that the pH values in these tests were quite acidic, it is expected that sorption/complexation of TcO_4^- was likely responsible for some uptake by the solid phase. Especially as it applies to the EMDF, it is also likely that some removal of TcO_4^- from the aqueous phase can be attributed to the OM reducing TcO_4^- into the strongly binding Tc^{4+} form. OM reduction of TcO_4^- was demonstrated using geological media collected from the Field Research Center on the ORR (Gu et al., 2011).

pH, iron- and manganese oxides, and organic matter interactions: TcO_4^- sorbs very weakly to soils, however sorption increases when groundwater pH decreases in the presences of OM, iron oxides, and manganese oxides (Kaplan, 2003). As described for I in section 3.1.3, decreases in system pH promotes protonation of the OM and oxides, thereby creating more positive surface charge sites for the anionic TcO_4^- species to bind. As pH values decrease below the zero-point-of-charge (ZPC), the amount of TcO_4^- sorbed to the solids increases. As noted in section 3.1.3, the pH values of the geological material suspensions (Table 3-1) are well below the ZPC for the oxides and organic matter expected at the EMDF.

3.3 Uranium K_d Values

3.3.1 Uranium K_d Value Results

Because uranium is naturally occurring, it was necessary to include controls to determine the amount of dissolved U in the test suspensions prior to adding the U spike for the K_d measurement. For 12 of the 14 sediments, the amount of aqueous U in the 1 g sediment and 25 mL groundwater suspension was <0.1 µg/L U, i.e., below the detection limit, the remaining two sediment suspensions contained 0.137 and 0.148 µg/L U (Appendix Table 5-7). These very low concentrations made it possible to use the depleted U standards as a spike solution without the need to correct for the presence of background U concentrations using Equation 1. The concentration in the aqueous phase at the start of the separate batch experiments was 42.3 µg/L U, generally,400 times greater than background.

Uranium K_d values were generally high, ranging from 622 to >10,165 mL/g, with a median of 5726 mL/g (Table 3-2). The median for the Maryville, Chestnut Ridge, and Nolichucky formations was >4567, 3959, and >6731 mL/g, respectively (Table 3-3). It was decided to present the sorption data also in terms of apparent solubility values in an effort to shed more light on the extraordinary large amount of U sorption suggested by the K_d values: generally about 10^{-9} moles/L (Table 3-1). These values are easy to misinterpret. They are U concentrations in the aqueous phase and are appropriate to use when solubility is controlling the partitioning of U between the solid and aqueous phases. Different experiments are typically conducted to measure solubility and to identify the phases responsible for controlling the solubility. For this reason, we elect to refer to this term simply as the apparent solubility value, to distinguish it from true single phase controlling solubility values.

3.3.2 Uranium K_d Value Compared to Previously Reported Values

The only previous measured U K_d values found in the literature were those reported by (Stewart et al., 2010). Unfortunately, while the study provided important insight about the importance of Ca and carbonate concentrations to U binding to Oak Ridge Melton Branch Ridgetop sediment, it provided little quantitative information regarding U binding to ORR sediments under PA relevant conditions. They reported U K_d values ranging from 0 to 95 mL/g, decreasing with the amount of Ca and/or carbonate included in the system, but they used more than 100 times more uranium (millimolar U concentrations) than we used in our studies (micromolar U concentrations) and only 3 days rather than 14 days to permit the system to come to steady state. Together, these experimental conditions would be less conducive to sediment binding of U than would be expected under EMDF conditions.

3.3.3 Discussion of potential geochemical processes responsible for uranium sorption in these experiments

Uranium binding to this sediment may be due in part to the natural existence of Fe(II) in Oak Ridge minerals. Also, the pH of the system is almost ideal for U immobilization. The extent of adsorption on Oak Ridge subsurface sediment increased sharply as the pH increased from 4.5 to 5.5, is at its maximum binding efficiency between pH 5.5 and 7.5, and then decreased sharply over the pH range of 7.5 to 8.5 as the concentration of dissolved carbonate and U(VI)-carbonate complexes increased ((Barnett et al., 2002; Barnett et al., 2000). There has been an unusually large amount of research on U redox chemistry in Oak Ridge sediments, primarily because the DOE was interested in evaluating whether redox manipulations of the subsurface environment could be used to immobilize groundwater U (Kelly et al., 2010; Li et al., 2019a; Spain and Krumholz, 2011). Zhong et al. (2005) showed that Oak ridge sediments could result in reductive precipitation of uranyl under natural conditions, but that the reduction was readily reversible. Iron oxide coatings on Oak Ridge sediments were shown to play an important role in uranyl uptake (Li et al., 2019b; Stewart et al., 2010). Increases in groundwater calcium concentration further decreased uranyl sorption to an Oak Ridge Melton Branch Ridgetop sediment (Stewart et al., 2010). Together, the high concentrations of iron and organic matter coatings, the near ideal pH for sorbing U, and the natural presence of Fe(II)-bearing minerals, may all contribute to promoting binding of U.

4.0 Conclusions

A summary of previously measured K_d values from ORR geological materials and those measured for this study are presented in Table 4-1. Also presented in Table 4-1 are the K_d values used in the 2020 PA for the EMDF (UCOR, 2020). The I K_d values reported in this study are consistent, but generally greater than those previously measured. The I K_d values in the 2020 PA, the bottom row in Table 4-1, were generally an order of magnitude less than the mean values measured in this study. The Tc K_d values reported here varied greatly between samples, with strong indication that TcO_4^- adsorption was not the only mechanism of uptake by these ORR geological materials. Instead, it appears very likely that half of the 10 materials evaluated promoted the reduction of TcO_4^- into the strongly binding and less soluble Tc^{4+} species. The implications of this are profound in terms of the natural attenuation of Tc that may be present, but not quantified, in the EMDF subsurface environment. Identifying the geological chemical and spatial limits, and carefully quantifying Tc^{4+} solubility under field conditions may provide an opportunity to reduce unnecessary conservatism in the PA. Similarly, the U K_d values measured in this study are much greater than those presently being used in the PA, 25 and 50 mL/g. There are some geological formation in ORR that have much higher pH of about pH 7.5 and greater carbonate concentrations than the selected EMDF location. These other formations may be expected to have low U K_d values that are similar in magnitude to those presently being used by the PA. As noted above, the lower pH (~pH 5), low carbonate, relatively high Fe(II)-mineral content, and organic matter are conditions that may be contributed to the elevated radionuclide uptake measured in this report. Finally, the I, Tc, and U K_d values measured in this study indicate that the corresponding K_d values used the 2020 PA were conservative.

Table 4-1. I, Tc, and U K_d values (mL/g) of ORR geological materials.

Iodine K_d (mL/g)		Tc K_d (mL/g)		U K_d (mL/g)		Comment
Mean	**Range**	**Mean**	**Range**	**Mean**	**Range**	
37.8	-1.8 – 140.9	365.7 [a]	-0.5 – >2678.3	5726 [a]	625 – 10,208	This study; Table 3-2 [a] Median, not mean, Tc and U K_d presented because of there being several unmeasurable (greater-than) Tc and U K_d values in this study.
17.1	3.6 – 54.4					(Rothschild et al., 1994)
11.7	1 – 21.4					(Davis et al., 1984)
		0.72	0.53 – 1.04			(DOE-OR, 1992)
		12.3	0.3 – 266			(Meyer et al., 1987) Study was conducted under alkaline conditions (pH 8.13) and therefore Tc is not expected to bind as much to the geological materials as would occur at the lower pH values measured at the EMDF site.
	2 [b] – 4 [c]		0.36 [b] – 0.72 [c]		25 [b] – 50 [c]	(UCOR, 2020); latest PA document. [b] K_d value used for Waste Zone [c] K_d value used for Vadose and Saturated Zone I $K_d = 0.2$ and Tc $K_d = 0.04$ and U $K_d = 3$ for screening model

5.0 References

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Appendix A. Supporting Data

Appendix Table 5-1. Iodine K_d values from geological samples collected from Solid Waste Storage Area 7 (data taken from Tables 6 and 7 in Rothschild et al. 1984).

Description[a]	**I- K_d (mL/g)**	**pH**	**Organic Matter (%)**	**Mn (mg/kg)**	**Fe (mg/kg)**	**Comment**
Sample 1	9.4	5	3.06	360	118	soil
Sample 2	4.7	6.2	4.15	715	151	soil
Sample 3	3.6	6	4.99	1160	250	soil
Sample 4	54.4	4.7	0.4	170.5	118	soil
Sample 5	12.3	4.5	2.06	169	120	soil
Sample 6	19.9	5.4	3.48	390	119	soil
Sample 7	14.8	4.7	3.43	655	245.5	soil
Sample 8	11.2	4.9	3.8	645	209	soil
Sample 9	20.1	4.9	2.01	153.5	78.5	soil
Sample 10	16.3	4.6	3.4	277.5	88.5	soil
Sample 11	17	5	2.84	367.5	112.5	soil
Sample 12	10.9	4.6	4.61	148.5	96.5	soil
Sample 13	37.7	4.9	3.25	28.5	41	taken from walls of drainageways
Sample 14	19.5	4.9	4.73	825	257	taken from walls of drainageways
Sample 15	4.4	4.6	3.48	109.5	83.5	taken from walls of drainageways
Average	**17.1**	**5.0**	**3.31**	**412**	**139**	
Std. Deviation	**13.4**	**0.5**	**1.2**	**321.9**	**68.5**	

[a] Three I-K_d values measured by Rothschild et al. (1984) for stream sediments are not reported in this table because their properties are not expected in the EMDF subsurface.

Appendix Table 5-2. Iodine K_d values of 24 soils collected from three cores recovered from Solid Waste Storage Area 6 (data taken from Table 7 in Davis et al. 1984).

Description (core ID/core depth-cm)	**Iodine K_d (mL/g)**	**pH**	**Organic Matter (wt%)**
334/20	21.4	4.3	1.4
334/40	18.5	4	1.4
334/60	22.8	4.2	0.26
334/100	2.2	4.4	0.15
334/130	1.1	4.4	0.14
334/150	4.2	4.3	0.11
334/180	10.5	4.3	0.11
334/200	11.3	4.3	0.11
338/20	4.1	4.4	1.24
338/40	11.1	4.4	0.83
338/60	1	4.3	0.3
338/100	18.6	4.4	0.16
338/130	0.3	4.4	0.11
338/150	3.8	4.6	0.27
338/180	2.6	4.7	0.09
338/200	0.1	5.8	0.11
342/20	10.1	4.4	0.41
342/40	14.8	4.3	0.45
342/60	13.8	4.6	0.21
342/100	23	4.3	0.29
342/130	14	4.2	0.28
342/150	31.7	4.3	0.12
342/180	24	4.3	0.2
342/200	16	4.2	0.07
Ave of 24 samples	**11.7**	**4.4**	**0.37**
Stdev of 24 samples	**9.0**	**0.3**	**0.41**

Appendix Table 5-3. Duplicate I, Tc, and U K_d values determined as part of this study.

SRNL Sample ID	Sample ID	Formation	Weathered Sediment/ Saprolite	Tc K_d (mL/g)	Iodine K_d (mL/g)	Uranium K_d (mL/g)
805a	ETP32-KD-6.5	Maryville	Weathered Sediment	15.0	107.7	8126.5
805b				2625.1	4.4	>10145.2
806a	ETP35-KD-8	Maryville	Weathered Sediment	7.3	88.5	>10134.6
806b				7.7	4.2	4290.5
803a	ETP27-KD-8.5	Maryville	Weathered Sediment	2630.9	13.7	8082.9
803b				2625.7	28.9	7625.7
809a	EBH42-KD-20	Maryville	Saprolite	452.4	12.6	1937.5
809b				298.8	75.8	1906.0
802a	EBH44-KD-20	Maryville	Saprolite	2621.3	2.7	607.4
802b				1042.6	9.1	636.4
804a	EBH43-KD-20	Maryville	Saprolite	171.0	5.8	1408.2
804b				540.6	-0.5	1560.4
807a	ETP51-KD-3	Chestnut Ridge	Weathered Sediment	7.4	127.5	3745.0
807b				2627.8	58.0	3917.7
801a	ETP43-KD-5	Chestnut Ridge	Weathered Sediment	0.6	196.9	4590.5
801b				2.3	85.0	3330.8
810a	ETP48-KD-6	Chestnut Ridge	Weathered Sediment	46.7	9.0	3961.2
810b				887.8	121.8	3953.0
808a	ETP49-KD-9	Chestnut Ridge	Weathered Sediment	1110.9	39.6	>10189.5
808b				1183.2	55.9	>10140.9
811a	HR-EMDF-1	Nolichucky	Weathered Sediment	0.5	1.0	6203.6
811b				-0.2	NA	5848.5
812a	HR-EMDF-2	Nolichucky	Weathered Sediment	-1.5	-1.8	5663.7
812b				2.2	2.7	5186.7
813a	BCR-EMDF-1	Nolichucky	Saprolite	2.5	4.4	4670.7
813b				2.1	0.4	>10202.3
814a	BCR-EMDF-2	Nolichucky	Weathered Sediment	-1.5	2.2	>10177.1
814b				0.5	1.1	6367.1

Appendix Table 5-4. Tc K_d values measured from shales samples recovered from near the WAG-1 area in Bethel Valley (data taken from Table A4.1.8 and geological media descriptions from page 10 of DOE-OR (1992)).

Tc Kd (mL/g)	Sample ID	Contact Time (Day)	Sample description[a]
1.04	01.SB103	1	#1
0.84	01.SB103	3	#1
0.79	01.SB103	14	#1
0.76	01.SB135	1	#2
0.67	01.SB135	3	#2
0.68	01.SB135	14	#2
0.53	01.SB184B	1	#3
0.59	01.SB184B	3	#3
0.61	01.SB184B	14	#3
0.72 ± 0.16	**Ave. ± Stdev.**		
0.53 to 1.04	**Range**		

[a] #1 - clay texture sediment, 8-9 ft interval from boring 01.SB103 adjacent to Impoundment 3513

#2 - predominant clay texture sediment, red/yellow & brown color; 24-25.8 ft interval from boring 01.SB135 located just south of Building 3019; "Explosion 2019"

#3 - clay texture sediment; yellow-brown; 6-8 ft interval from boring 01.sb184B located at the southeast corner of Building 3525; "Leak 3525"

Appendix Table 5-5. TcO_4^- K_d values to shale samples (Rs = K_d data taken from Table 4.13 in Mayer et al. 1987).

Shale	Groundwater[a]	Final pH	K_d (mL/g)
Upper Dowelltown	diluted brine	3.54	266 ± 18.1
	bicarbonate	8.42	14.8 ± 1.1
Pierre	diluted brine	NA	3.0 ± 0.7
	bicarbonate	8.52	1.7 ± 0.4
Green River Formation	diluted brine	NA	1.8 ± 0.0
	bicarbonate	9.09	0.3 ± 0.3
Nolichucky	diluted brine	NA	1.2 ± 0.3
	bicarbonate	9.61	1.3 ± 0.3
Pumpkin Valley	diluted brine	NA	0.9 ± 0.5
	bicarbonate	9.59	1.0 ± 1.0

[a] The Tc K_d suspensions consisted of 0.2 g shale and 2 mL of groundwater with an initial TcO_4^- concentration of 10 nmol/L. The contact time of the Tc with the solids was 19 days. The groundwater was either a dilute brine (34.1 mM/pH 5.0 artificial brine solution) or a bicarbonate (30 mmol sodium bicarbonate solution/pH 9.6).

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Appendix Table 5-6. Field notes recorded by samplers for the Nolichucky samples.

Location	Sample ID	Approx. Depth (ft)	Description	Priority for analysis
South side of Haul Road, west of UPF spoils entrance, directly across from speed limit sign on North side of HR	HR-EMDF-1	3-4	Clay rich material in contact with underlying weathered shale	Priority 1, homogenize entire sample to extent possible and obtain representative subsamples
South side of Haul Road, west of UPF spoils entrance, directly across from speed limit sign on North side of HR	HR-EMDF-2	3-4	Clay rich material	Priority 2, homogenize entire sample to extent possible and obtain representative subsamples
North side of Bear Creek Road, between GW-998/999 and GW-996/997	BCR-EMDF-1	5	Weathered shale fragments with some fine-grained material	Priority 1, pulverize representative portion of shale fragments for analysis
North side of Bear Creek Road, between GW-998/999 and GW-996/997	BCR-EMDF-2	5	Clay rich material (could be material from shallower depth)	Priority 2, homogenize entire sample to extent possible and obtain representative subsamples

Appendix Table 5-7. Sediment and groundwater suspensions uranium concentrations prior to adding uranium spike. Control samples to provide a measure of the background uranium concentrations. (25 mL groundwater, 1 g sediment, 2-week equilibration period, ICP-MS analysis of aqueous phase after phase separation by filtration).

Sample ID	Sediment	U (ug/L)
U801C-Control	801	<1.00E-01
U802C-Control	802	1.48E-01
U803C-Control	803	<1.00E-01
U804C-Control	804	1.37E-01
U805C-Control	805	<1.00E-01
U806C-Control	806	<1.00E-01
U807C-Control	807	<1.00E-01
U808C-Control	808	<1.00E-01
U809C-Control	809	<1.00E-01
U810C-Control	810	<1.00E-01
U811C-Control	811	<1.00E-01
U812C-Control	812	<1.00E-01
U813C-Control	813	<1.00E-01
U814C-Control	814	<1.00E-01

Appendix Table 5-8. Second Groundwater (GW-989) chemical properties.

Property (unit)	Value	Measurement [a]
Nitrate (μg/L)	209	Lab Measurement: EPA-300.0
Chloride (μg/L)	1630	Lab Measurement: EPA-300.0
Sulfate (μg/L)	19400	Lab Measurement: EPA-300.0
Bicarbonate (μg/L)	201000	Lab Measurement: EPA-310.1
Carbonate (μg/L)	4000	Lab Measurement: EPA-310.1
Dissolved Solids (μg/L)	224000	Lab Measurement: SM-2540 C
Dissolved Organic Carbon (μg/L)	1230	Lab Measurement: SM-5310 B
[a] Lab measurements were conducted at GEL Laboratories, LLC, Charleston, SC by the standard methods noted (APHA, 2005; EPA, 2019a, b).		

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