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Determination of constituent concentrations in field lysimeter effluents Connor Parker and Brian A. Powell

## FY20 Report

## SRR Project Title: SRR Technical Support Provided by Clemson University SRR PO number: SRRA021685SR

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## ABBREVIATIONS

BFS	Blast Furnace Slag
CDB	Citrate-Bicarbonate-Dithionite
CEC	Cation Exchange Capacity
DDI	Distilled Deionized Water
DO	Dissolved Oxygen
EDTA	Ethylenediaminetetraacetic acid
FY12Q4	Fiscal Year (YY) Quarter (Q)
HDPE	High-density Polyethylene
HNO <sub>3</sub>	Nitric Acid
HPGe	High Purity Germanium Detector
ICP-MS	Inductively Coupled Plasma Mass Spectrometer
ID	Identification
LLD	Lower Limits of Detection
MDC	Minimum Detectable Concentration
NA	Not available; no measurement because sample volume was too small
NOM	Natural Organic Matter
NIST	National Institute of Standards and Technology
OM	Organic Matter
ppb	Parts per billion
ppm	Parts per million
PA	Performance Assessments
PVC	Polyvinyl Chloride
QA/QC	Quality Assurance and Quality Control
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation LLC
SRS	Savannah River Site
VWR	VWR Inc. (chemical and laboratory supplies)
XRD	X-Ray Diffraction

## EXECUTIVE SUMMARY

This report summarizes the effluent measurements of the RadFLEx (Radiological

Field Lysimeter Experiment) being run at the Savannah River Site (SRS). The facility

was opened in May 2012 and effluent measurements have been performed on a quarterly

basis since October 2012. A variety of radionuclide sources were present when the field

lysimeter program was initiated, including:

Homogenous sources (oxides or solution deposited)

- Six Pu<sup>V</sup>NH<sub>4</sub>(CO<sub>3</sub>): three with natural organic matter (NOM) added and three without NOM
- Three solution deposited beta/gamma emitters, <sup>137</sup>Cs, <sup>60</sup>Co, <sup>133</sup>Ba, and <sup>152</sup>Eu
- Two NpO<sub>2</sub> and two NpO<sub>2</sub>NO<sub>3</sub>
- Six  $Pu^{IV}(C_2O_4)_2$  sources: three with grass on the surface and three without
- Three  $Pu^{III}_2(C_2O_4)_3$  sources
- Three Pu colloids (PuO<sub>2</sub>)
- Four sediment controls with no radionuclides

Cementitious sources:

- Four radionuclide-free cementitious material (control)
- Six (3 cement, 3 grout) gamma emitters,  $^{137}Cs$ ,  $^{60}Co$ ,  $^{133}Ba$ , and  $^{152}Eu$
- Four (2 cement, 2 grout) <sup>99</sup>Tc and I (no longer active, two have been removed and two are capped in place)

For convenience, all data from previous years have been included in this report and the

data from July 2019-March 2020 have been added. Note that the <sup>99</sup>Tc bearing lysimeters

were either capped or removed in 2013. Therefore, there is no discussion of these

lysimeters in this report.

The most relevant results observed in FY20 are as follows:

• The concentration of Pu in lysimeter effluents collected from the 190716

sampling event were on the order of  $10^{-15}$  to  $10^{-13}$  mol/L, as determined using a

pre-concentration step and ultra-low-level counting approach. Direct measurements using ICP-MS were at or below detection limits.

- Newly installed lysimeters L14-2, L20-2, and L21-3 which contain Pu(V) sources and are amended with natural organic matter have shown breakthrough of Pu on the order of 10<sup>-11</sup> to 10<sup>-12</sup> M which was detectable directly using ICP-MS.
- Lysimeters 29 and 30 containing NpO<sub>2</sub>NO<sub>3</sub> sources have measurable breakthrough corresponding to 1,558 Bq and 17,627 Bq (Note: Lysimeter 29 was removed in 2015 and was replaced with a new NpO<sub>2</sub>(s) source in 2019). These values correspond to 3% and 37% of the initial source activity assuming a 45.88 kBq initial source<sup>1</sup>. The variability in these numbers is hypothesized to be caused by heterogeneous flow of water through the lysimeter. <sup>237</sup>Np was also observed in the effluent of lysimeters 31 and 32 which contained relatively insoluble NpO<sub>2</sub> source. Lysimeter 31 was removed in 2015 and destructively sampled after 0.3 Bq had been eluted. Lysimeter 32 has been continuously deployed and as of March 2020, 51.2 Bq has been eluted. The observation of Np in the effluent from lysimeters 31 and 32 imply that the NpO<sub>2</sub> is becoming oxidized and releasing Np<sup>V</sup> which can transport through the lysimeter with a relatively low K<sub>d</sub>.

<sup>&</sup>lt;sup>1</sup> Evaluation of multiple NpO<sub>2</sub>(s) sources indicates some variability in the total <sup>237</sup>Np content in each source despite a similar level reported by Roberts et al. (2012). The variability is likely due to the difficulty of weighing small aliquots of solid actinide sources within a HEPA filtered glovebox at Savannah River National Laboratory. Thus, a better approach is to compare total activity leached and aqueous concentrations of each radioisotope in the effluent waters to evaluate the potential for solubility control of the aqueous concentration.

- Activities of <sup>60</sup>Co were initially measured above detection limits in the effluent of • all lysimeters containing saltstone or cement sources. However, in recent sampling events, some saltstone bearing lysimeters (L16) were below <sup>60</sup>Co detection limits. Lysimeter containing only soil with the gamma isotopes deposited onto a filter paper were below detection limits (Lysimeters 27 and 28). Note that the sediment controls also contained ~100x lower total activity compared with the saltstone or cement source lysimeters. However, the concentrations were much lower than previous sampling events. The majority of the <sup>60</sup>Co was released within the first 2 years of the experiment and concentrations are now close to detection limits. All cement and saltstone lysimeter sources contained higher concentrations of <sup>60</sup>Co in the effluent relative to a control (filter paper only containing the radioisotopes), in which the gamma suite of radionuclides was added directly to a filter. However, the control lysimeter contained approximately 20× lower total activity of each radioisotope. Thus, given the potential uncertainty in the source term concentrations (see footnote 1 on page 8), it is possible that similar fractions of <sup>60</sup>Co are being transported in the control, cement, and saltstone source lysimeters.
- There is a high degree of variability in the amount of water flowing through each lysimeter. It is hypothesized this is due to heterogeneous flow of water through the soil and variations in the localized weather (i.e. wind and rain patterns) above the lysimeter openings.

### 1. INTRODUCTION

This document describes the analysis of the effluent from lysimeters from the Radiological Field Lysimeter Experiment (RadFLEx) facility discussed in the report "SRNL Radionuclide Field Lysimeter Experiment: Baseline Construction and Implementation" by Roberts et al. (2012, SRNL-STI-2012-00603). Savannah River National Laboratory (SRNL) presently has multiple active experiments at the RadFLEx facility to investigate radionuclide transport under field conditions. In this experiment, radionuclides are buried in 5-L containers that are open to precipitation. Leachate is collected from these lysimeters approximately every three months to provide a measure of radionuclide transport through the 24" long columns. Ten lysimeters contain cementitious sources. Several lysimeters were removed from service prior to fiscal year (FY)20 to quantify the concentrations of radionuclides within the soil as a function of depth and also to characterize chemical and physical changes to the source material that may have occurred during exposure to natural conditions. Although these solid phase analyses are complete for some lysimeters, discussion of the resulting data is outside the scope of this report.

At the start of FY20, there were 29 active lysimeters. The lysimeters contain either a cementitious waste form as a source or a "soil" source. The soil sources are made by placing the radionuclide source between two filter papers and placing the filter paper in direct contact with the soil mid-way up the lysimeter. The cementitious waste form sources are 1.25" diameter cementitious "pucks" containing the radionuclides of interest which are also placed midway up the lysimeter. The active lysimeters are:

## Cementitious waste form lysimeters

- Radionuclide-free cementitious material controls (lysimeters 3 and 15). Note lysimeter 15 was capped in May 2018 and uncapped in June 2018.
- A suite of gamma emitters, <sup>137</sup>Cs, <sup>60</sup>Co, <sup>133</sup>Ba, and <sup>152</sup>Eu (lysimeters 4-6 and 16-18). Note lysimeters 5, and 16 were removed on 9/8/2016 for non-destructive testing and redeployed on 04/20/2017. Lysimeter 4 was also removed for non-destructive testing on 10/8/2015 and redeployed on 4/20/2017.

Soil source lysimeters

- Pu<sup>V</sup>NH<sub>4</sub>(CO<sub>3</sub>) (lysimeters 22, 23, and 42,43).
- A suite of beta/gamma emitters, <sup>137</sup>Cs, <sup>60</sup>Co, <sup>133</sup>Ba, and <sup>152</sup>Eu (lysimeters 26-28) deposted on filter papers. Note lysimeter 26 was removed on 9/8/2016 for non-destructive testing. At the conclusion of testing, the lysimeter was cut open at Clemson and shipped back to SRNL for analysis on 3/24/2017. Lysimeter 28 was capped in May 2018 and uncapped in June 2018.
- $Np^{V}O_2NO_3$  and  $Np^{IV}O_2$  (lysimeters 30 and 32)
- Pu<sup>III</sup><sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> and Pu<sup>IV</sup>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub> (lysimeters 9, 10, 11, 34, 35, 39, and 40). Note lysimeter 9 was capped in May 2018 and uncapped in June 2018.
- Pu<sup>IV</sup>O<sub>2</sub> colloids (lysimeters 45 and 46). Note lysimeter 45 and 46 were capped in May 2018 and uncapped in June 2018.
- Sediment controls with no radionuclides (lysimeters 12, 24, 25, and 37).

Lysimeters removed from RadFLEx for soil analysis in previous years are:

Soil source lysimeters

- Pu<sup>V</sup>NH<sub>4</sub>(CO<sub>3</sub>) lysimeters 21 and 41 removed in October 2014
- Np<sup>V</sup>O<sub>2</sub>NO<sub>3</sub> and Np<sup>IV</sup>O<sub>2</sub> lysimeters 29 and 31, respectively, removed November 2015
- Pu<sup>III</sup><sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> and Pu<sup>IV</sup>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub> 33 and 38, respectively, removed November 2015
- Pu<sup>IV</sup>O<sub>2</sub> colloids lysimeter 44, removed November 2015.
- Lysimeter 26 containing the suite of gamma emitters <sup>137</sup>Cs, <sup>60</sup>Co, <sup>133</sup>Ba, and <sup>152</sup>Eu deposited on a filter paper was removed 9/8/2016 for non-destructive measurements at Clemson. The lysimeter was then cut open and shipped back to SRNL for soil analysis on 3/24/2017.

New lysimeter sources added in FY20 were:

- Lysimeter 8-2: New NpO<sub>2</sub>(s) source
- Lysimeter 9-2: Ra-226 nitrate salt source in sand
- Lysimeter 14-2: New Pu(V)NH<sub>4</sub>CO<sub>3</sub> source with organic matter amendment
- Lysimeter 20-2: New Pu(V)NH<sub>4</sub>CO<sub>3</sub> source with organic matter amendment
- Lysimeter 21-3: New Pu(V)NH<sub>4</sub>CO<sub>3</sub> source with organic matter amendment
- Lysimeter 26-2: Ra-226 nitrate salt source in sand
- Lysimeter 29-2: New NpO<sub>2</sub>(s) source

- Lysimeter 31-2: New NpO<sub>2</sub>(s) source
- Lysimeter 33-2: New Np(V)-nitrate source
- Lysimeter 36: Ra-226 nitrate salt source in sand
- Lysimeter 38-3: New Pu(V)NH<sub>4</sub>CO<sub>3</sub>(s) source in sand
- Lysimeter 41-3: New Pu(V)NH<sub>4</sub>CO<sub>3</sub>(s) source in sand
- Lysimeter 44-3: New Pu(V)NH<sub>4</sub>CO<sub>3</sub>(s) source in sand
- Lysimeter 47-2: Grout Mix1/Iodine/L3
- Lysimeter 48-2: Grout Mix1/Iodine/Ag/L3

Two lysimeters (24 and 37) were constructed to be used as instrumental controls.

These lysimeters were prepared identically to the other lysimeters except no source was added. These instrumented control lysimeters were fitted with two Decagon 5TM probes, which measure soil moisture and temperature, located 20 cm and 51 cm from the top of the lysimeters. Additionally, each lysimeter was fitted with one Decagon 5TE probe, which measures soil moisture, temperature and electrical conductivity, located 36 cm from the top of the lysimeters. All of the probes collect data every 30 minutes. The data is collected during sampling of the lysimeter effluent. Another Decagon 5TE probe was placed in the soil at the site to monitor actual conditions in the field (Roberts et al., 2012).

## 2. DATA REPORTING and TIMEKEEPING

In previous reports the data were described based on the FY and quarter (Q) in which samples were collected. This was a convenient method at the time but inherently caused problems when sampling events are missed or there are multiple sampling events in one quarter. Therefore, in this report the current sampling events are described using the date of sampling. For example, samples collected on July 14, 2015 are labeled 150714. This is the sampling ID protocol being used by Savannah River National Laboratory (SRNL) collaborators when collecting the field samples. Therefore, to maintain consistent records, a list of sampling dates, SRNL sample IDs, and the ID used in this report to note the entire sampling event are provided in Table 2.1. The electronic database accompanying this report uses this same ID format (described below).

Sampling Date(s)SRNL Sample ID range (notation is year-month-date of sample collection)		ID used in this report to describe sampling event (ID used in previous reports)		
10/4/2012	121004	100412 (FY13Q1)		
1/9/2013	130109	130109 (FY13Q2)		
3/7/2013	130212-130307	130212-130307 (FY13Q3)		
6/13/2013	130514-130617	130514-130617 (FY13Q4)		
11/5/2013	131105-131106	131105-131106 (FY14Q1)		
2/10/2014	140210	140210 (FY14Q2)		
5/5/2014	140505	140505 (FY14Q3)		
7/16/2014	140716	140716 (FY14Q4)		
11/5/2014	141105	141105		
1/6/2015	150106	150106		
3/26/2015	150326	150326		
7/14/2015	150714	150714		
10/8/2015	151008	151008		
12/16/2015	151216	151216		
3/1/2016	160301	160301		
6/1/2016	160601	160601		
8/9/2016	160809	160809		
2/7/2017	170207	170207		
08/02/17-08/03/17	170802-170803	170802-170803		
11/20/2017*	171120	171120		
1/10/2018	180110	180110		
3/8/2018*	180308	180308		
4/11/2018*	180411	180411		
6/27/2018	180627	180627		
9/10/2018**	180910	180910		
10/16/2018**	181016	181016		
11/26/2018**	181126	181126		
12/19/2018	181219	181219		
2/4/2019**	190204	190204		
3/7/2019**	190307	190307		
5/22/2019	190522	190522		
7/16/2019	190716	190716		
1/22/2020	200122	200122		
3/11/2020 200311		200311		
*only Lys. 30 was sampled in this event **only 30 & 32 were sampled in this event				

Table 2-1: List of Sample dates and IDs from RadFLEx effluent sampling.

### 3. BACKGROUND

#### Project overview

Understanding the geochemical behavior and vadose zone transport of radionuclides produced during nuclear weapons development and generated during nuclear power production is very important when determining a long-term storage solution for radioactive waste. Long-lived actinides, such as neptunium and plutonium (predominantly <sup>237</sup>Np and <sup>239</sup>Pu), as well as the fission products, <sup>137</sup>Cs and <sup>99</sup>Tc, are risk driving radionuclides under release or disposal scenarios due to their long half-lives, environmental mobility, or quantity. Subsurface transport of these elements is influenced by many factors including sorption, oxidation and reduction, complexation, and precipitation reactions (Choppin, 2006; Cleveland, 1979; Kaplan et al., 2006a and 2006b; Kaszuba and Runde, 1999; Kim et al., 2006; Madejon, 2012). A greater understanding of this behavior will help to develop more robust geochemical models and reduce conservatism in performance assessments (PAs). Laboratory experiments provide valuable data but there is a need to supplement this data with field scale experiments that can be performed under more representative environmental conditions. For example, several studies have examined the transport of plutonium using field lysimeters and used lab scale data to conceptualize the field scale reactive transport models (Kaplan et al., 2004; Kaplan et al., 2006a and 2006b).

Lysimeters are columns packed with soil or sediment that contain a source amended with a radionuclide of interest placed at the midpoint of the column. The lysimeters are left exposed to rainfall and field conditions. The effluent is collected and analyzed for the radionuclide initially amended in the source. Following a defined timescale for effluent collection, the lysimeters are cored and concentrations of radionuclide(s) in the soil/sediment phase are determined.

Early studies by Kaplan et al. (2004, 2006a, 2006b) provided valuable information about plutonium behavior in the vadose zone. The lysimeters contained sources of a known activity and oxidation state of plutonium and were left exposed to environmental conditions for approximately 2 and 11 years. The majority (>95%) of the plutonium remained within 2 cm of the source and in the Pu<sup>IV</sup> oxidation state, which is consistent with the expected redox conditions of the experiment and lower mobility of Pu<sup>IV</sup> relative to other Pu oxidation states (i.e., Pu<sup>V</sup> and Pu<sup>VI</sup>). Another important discovery from these works was the observed upward migration of plutonium. Demirkanli et al., (2008, 2009) and Thompson et al., (2012) provided strong evidence that this upward migration was caused by uptake in grass roots that grew naturally on the surface of the lysimeters during the experiment. More accurate simulations were developed by including partitioning coefficients between plutonium and the grass roots (Demirkanli et al., 2009). Laboratory studies of plutonium uptake and mobility in corn were also performed and provided additional support for this explanation (Thompson et al., 2012). The RadFLEx facility was designed to address the knowledge gaps from the previous work with the Pu-bearing lysimeters mentioned above, and RadFLEx initially deployed 43 lysimeters with controls or radionuclide-bearing sources (Roberts et al., 2012).

#### Soil and effluent characterization

The primary purpose of this project is to analyze samples from the RadFLEx facility, interpret the data, and provide any necessary explanation and support for the findings. The experiment began in May 2012 and is expected to span a ten-year period. This work includes measurements of quarterly effluent sampling events and analysis of any radionuclides measured in appreciable quantities during this period. Several lysimeters were removed for solid phase analysis and there are currently 46 active lysimeters as described in Section 1 "Introduction". Leachate is collected from these lysimeters every three months to provide a measure of radionuclide transport through the columns. Lysimeters containing plutonium sources were installed in triplicate so that soil profile analyses can be performed at three discrete time intervals. Analysis was only performed after 2 and 11 years during the original Kaplan et al. (2004, 2006a) study.

The RadFLEx facility is located at SRS in Aiken, SC. Each lysimeter (24" long, 4" diameter) has a volume of 4,118.5 cm<sup>3</sup> (1.09 gallons) that is open at the top-end allowing exposure to environmental conditions (Roberts et al., 2012). The lysimeters are all packed with a single, homogenized soil from the SRS which is representative of the endmember soil found at SRS. Specific chemical and physical characteristics of the soil are shown in Table 3.1 (Roberts et al., 2012). Additional mineralogical and elemental characterization was performed previously and is presented in Tables 3.2 and 3.3. The primary mineral phases are kaolinite and quartz. Unexpectedly, no goethite or hematite was observed in the powder x-ray diffraction (XRD) pattern. This is despite a relatively high iron content in the soil. It is hypothesized that the iron content is present as small disordered phases as coatings on quartz particles or incorporated into phyllosilicates.

However, this proposed iron mineralogy remains to be proven.

<b>Table 3-1:</b>	Characterization of soil obtained from Central Shops Borrow pit at the
	Savannah River Site (Roberts et al., 2012).

Analysis	Lysimeter Soil	Lysimeter Soil +OM <sup>1</sup>				
pH	5.27	4.89				
Organic-Carbon (%)	0.085	1.704				
Organic-Nitrogen (%)	0.008	0.062				
Organic-Sulfur (%)	0.012	0.018				
Sand $(\%)^2$	66	Not Meas.				
Silt (%) <sup>2</sup>	14	Not Meas.				
Clay $(\%)^2$	20	Not Meas.				
Surface Area (m <sup>2</sup> g <sup>-1</sup> )	9.14	Not Meas.				
CEC <sup>3</sup> (meq 100g <sup>-1</sup> )	1.73	5.56				
Base Saturation (%)	27.62	14.21				
$CDB^4$ Fe (mg g <sup>-1</sup> )	$6.01\pm0.68$	$\rm NM^5$				
CDB Al (mg $g^{-1}$ )	$1.978\pm0.20$	$NM^5$				
Total Fe (ppm)	8,101	13,180				
Total Mn (ppm)	7.29	7.72				
Total P (ppm)	36.6	<6				
Total S (ppm) 112.2 111.5						
<sup>1</sup> OM = organic matter, amended in the soil of lysimeters 21, 22, and 23.						
$^{3}CEC = Cation exchange capacity$						

<sup>4</sup>**CDB** = Citrate-Bicarbonate-Dithionite extractable

<sup>5</sup>NM = Not measured

 Table 3-2: Mineralogical fractions determined using powder X-ray diffraction by The Mineral Lab, Inc. (Golden, CO).

Phase	Whole Soil	<2um size fraction
Kaolinite	58	>95
Quartz	39	<2
Unknown	<5	<5

Phase	Percentage
MgO	0.14
Al <sub>2</sub> O <sub>3</sub>	13.6
SiO <sub>2</sub>	72.9
K <sub>2</sub> O	0.09
CaO	0.08
TiO <sub>2</sub>	0.47
Fe <sub>2</sub> O <sub>3</sub>	2.64
BaO, MnO <sub>2</sub> , Cl, S, P <sub>2</sub> O <sub>5</sub> , Na <sub>2</sub> O	< 0.05%

Table 3-3: Elemental X-ray Fluorescence analysis of soil composition. The balance of the percentages (approximately 10%) is due to chemically and physically sorbed water and other trace minerals.

### 4. MATERIALS AND METHODS

#### Lysimeter Design

The construction of the lysimeters used in this experiment is described in Roberts et al., 2012. The lysimeters are made from 24" length by 4" diameter polyvinyl chloride (PVC) pipes. A 4" to 2" reducer is placed at the bottom of the pipe to hold a perforated polypropylene grid supporting a nylon mesh screen (80 x 80 mesh, McMaster Car part # 9318T17) meant to prevent sediment from passing through into the effluent collection bottles. The 4" to 2" reducer is connected to a 2" bushing which is fitted with a  $\frac{3}{4}$ " barbed nipple. Nylon Tygon tubing is attached to the nipple to guide the effluent water into the collection bottles. Based on calculations using the average volume of water passing through the lysimeters, there should be no restriction of flow through this configuration. The lysimeters are housed in a 6" diameter PVC pipe with a 6" to 4" reducing bushing for the purpose of secondary containment. A small section of 4" PVC is glued into the bushing and coupled to another 4" to 2" reducer with a 2" PVC pipe that collects effluent for the secondary containment. The secondary containment serves not only as double containment consistent with radiological protection but also as a collection mechanism should any overflow occur from the lysimeters. A secondary but very important benefit of this design is that extraction of the lysimeters can be accomplished with relative ease. Images of the lysimeter components and schematic are shown in Figures 4.1 and 4.2, respectively.



Figure 4-1: Design components of the lysimeters (Roberts et al., 2012).



Figure 4-2: Schematic of the lysimeters. The nylon mesh was glued to the bottom of the PVC pipe. Then the polypropylene grid was glued on the bottom of the PVC pipe. Finally, 4" to 2" reducer was fitted over the bottom of the pipe. The purpose of the reducer was also to keep the nylon mesh and grid in place.

### Data Recording

All measurements and observations were recorded in a laboratory notebook with the appropriate title, time, date, and apparatus used. A sample data log sheet, that includes the unique sample and subsample code identification (ID), dates of sample collection, receipt from SRS and dates of sample preparation and analysis at Clemson, was created for each received sample. Preliminary measurements and subsampling information were also recorded on these data log sheets. An example data log sheet can be found in Appendix A.

The high purity germanium detectors (Model: GC2519, SN: 08017390 and Model: GC4018, SN: 1933074) and Thermo Scientific inductively coupled plasma mass spectrometer (ICP-MS) (Model: X-2, SN: 012990) were calibrated with National Institute of Standards and Technology (NIST) traceable standards. The calibration date, standard identification and expiration dates, and quality assurance and quality control (QA/QC) spiked samples were recorded on a calibration datasheet for each sampling event. An example datasheet for calibration can be found in Appendix A.

### Sample Receipt and Subsampling

Lysimeter effluent samples have been received in 2 L bottles on a quarterly basis since October 2012. Effluent samples are collected and shipped by SRNL collaborators Dr. Dan Kaplan and Dr. Kimberly Roberts. The methods described below have been used for the samples that have been received to this point and will be used for future samples. Approximately 250 mL, (or half of the total volume if the sample volume was less than 500 mL) of each lysimeter effluent sample was removed for archiving and placed into a 250 mL high-density polyethylene (HDPE) pre-cleaned container. The ID given to each subsample was also used for the archived containers. The pH and dissolved oxygen (DO) content of each received solution was measured using a Thermo Ross semi-micro pH electrode and an HI9142 (Hanna Instruments) DO probe. The pH electrode was standardized with Thermo pH buffer solutions at pH values of 4.01, 7.00 and 10.01. Archive information and pH and DO measurements were recorded on subsample data log sheets.

Lysimeter effluent bottles were acidified to 2% nitric acid (HNO<sub>3</sub>) using concentrated nitric acid. The intent of acidifying the solutions within the leachate collection bottles was to facilitate desorption of any ions sorbed to the container walls. Thus the 250 mL archived subsample removed is to preserve the sample in the "field" (non-acidified) state in the event that analysis of radionuclide speciation is to be performed at a future date. Samples for analyte measurements were taken from the acidified sample. In the event that there was a measurable quantity of a radionuclide in the acidified subsample, then inferences based on conceptual knowledge of radionuclide speciation could be made. For example, if plutonium was identified in the acidified subsample from a lysimeter containing a Pu source, but not in the un-acidified subsample, it could be assumed that Pu in the un-acidified bottle was in the +4 oxidation state, because Pu<sup>IV</sup> exhibits a high sorption affinity. Pu concentrations in the original, unacidified subsample could then be deteremined with dilution calculations. Additionally, oxidation state analysis of the acidified sample could verify these inferences. Any samples and subsamples taken from the acidified bottles were referred to as the sample ID with the suffix –Acid in subsample containers and data files.

### Minimum Detectable Concentrations

The lower limits of detection (LLD) were determined for each radionuclide. The LLDs were then used to calculate the minimum detectable concentrations (MDCs) using

the Currie Equation (Equation 1). The MDC calculated for radionuclides in this work,

for each sampling event, are reported in Table 4.1

$$MDC = \frac{LLD}{\epsilon \times t \times f \times V}$$
 (Currie, 1968) (1)

LLD = Lower limit of detection (counts)  $\epsilon = \text{efficiency}(-)$  t = count time (s) f = Branching ratio (-)V = Volume of subsample (L)

Sampling Event	<sup>60</sup> Co <sup>a</sup>	$^{137}Cs^a$	$^{133}\mathrm{Ba}^{a}$	<sup>152</sup> Eu <sup>a</sup>	$^{237}\mathrm{Np}^{b}$	$^{239/240}$ Pu <sup>b</sup>
121004	4.98E+01	3.77E+00	2.92E+00	4.66E+01	ND	ND
130109	3.81E+00	5.17E+00	1.12E+01	1.42E+02	ND	ND
130212- 130307	3.97E+00	4.26E+00	1.21E+01	1.52E+02	1.49E-01	9.86E-02
130514- 130617	3.97E+00	4.99E+00	1.21E+01	1.52E+02	8.34E-04	2.45E-01
131105- 131106	6.10E+00	5.80E+00	9.43E+00	1.33E+02	2.60E-04	1.38E-01
140210	4.52E+00	5.66E+00	1.09E+01	1.58E+02	1.48E-03	1.72E-01
140505	5.39E+00	7.31E+00	1.39E+01	1.71E+02	4.69E-04	1.58E-01
140716	4.22E-02	7.08E-02	1.26E-01	1.66E+00	2.45E-03	2.39E-01
141105	1.27E+00	1.35E+00	2.56E+00	3.14E+01	4.17E-04	9.18E-02
150106	2.28E+00	2.58E+00	5.47E+00	7.73E+01	1.00E-04	6.58E-01
150326	2.28E+00	2.58E+00	5.47E+00	7.73E+01	1.00E-04	6.58E-01
150714	1.42E+00	3.94E+00	5.00E+01	1.57E+02	1.26E-04	5.28E-02
151008	1.35E+00	1.44E+00	2.78E+02	3.36E+01	6.80E-05	8.70E-05
151216	1.35E+00	1.44E+00	2.78E+02	3.36E+01	6.80E-05	8.70E-05
160301	1.81E+00	6.31E+00	2.31E+02	8.06E+01	2.50E-05	8.24E-04
160601	3.43E+00	6.42E+00	1.86E+02	4.28E+02	4.40E-05	2.50E-05
160809	2.67E+00	1.99E+00	5.11E+00	6.86E+01	2.82E-04	1.48E-03
170207	4.09E+00	5.85E+00	1.00E+01	1.22E+02	1.90E-05	3.00E-06
170802-						
170803	4.31E+00	6.29E+00	1.09E+01	1.37E+02	2.24E-04	2.70E-05
171120	ND	ND	ND	ND	1.10E-05	3.00E-06
180110	5.00E+00	6.03E+00	1.03E+01	1.32E+02	7.70E-05	1.14E-04
180308 <sup>c</sup>	ND	ND	ND	ND	7.70E-05	ND
180411	3.41E+00	4.13E+00	7.68E+00	8.94E+01	1.00E-03	1.04E-03
180627	3.41E+00	4.13E+00	7.68E+00	8.94E+01	1.00E-03	1.04E-03
180910	4.62E+00	5.45E+00	9.72E+00	1.11E+02	1.00E-03	1.00E-03
181016	4.62E+00	5.45E+00	9.72E+00	1.11E+02	1.00E-03	1.00E-03
181126	4.62E+00	5.45E+00	9.72E+00	1.11E+02	1.00E-03	1.00E-03
181219	4.62E+00	5.45E+00	9.72E+00	1.11E+02	1.00E-03	1.00E-03
190204	4.62E+00	5.45E+00	9.72E+00	1.11E+02	1.00E-03	1.00E-03
190307	4.62E+00	5.45E+00	9.72E+00	1.11E+02	1.00E-03	1.00E-03

 Table 4-1: Minimum detectable concentration calculated for effluent analysis. ND: Not determined.

Sampling Event	<sup>60</sup> Co <sup>a</sup>	$^{137}\mathrm{Cs}^{a}$	$^{133}\mathrm{Ba}^{a}$	$^{152}\mathrm{Eu}^{a}$	$^{237}\mathrm{Np}^{b}$	$^{239/240}$ Pu <sup>b</sup>	
190522	4.62E+00	5.45E+00	9.72E+00	1.11E+02	1.00E-03	1.00E-03	
190716	4.62E+00	5.45E+00	9.72E+00	1.11E+02	1.00E-03	1.00E-03	
200122	4.72E+00	4.01E+00	9.62E+01	8.37E+00	1.00E-03	1.00E-03	
200311	4.72E+00	4.01E+00	9.62E+01	8.37E+00	1.00E-03	1.00E-03	
<sup><i>a</i></sup> Values based on background count rate and efficiency in the region of interest of the gamma energy for the respective isotope. Values reported in Bq L <sup>-1</sup>							
<sup>b</sup> Values based on ICP-MS intercept concentration values reported in ppb ( $\mu$ g L <sup>-1</sup> ).							
<sup>c</sup> Only <sup>237</sup> Np measured for these samples because only samples from Lysimeter 30 were received							

## Analysis of Gamma Emitting Radionuclides (<sup>60</sup>Co, <sup>137</sup>Cs, <sup>133</sup>Ba, <sup>152</sup>Eu)

Samples containing gamma emitting radionuclides were analyzed using a high purity germanium detector (HPGe). One HPGe (Model: GC4018, SN: 1933074) was used for analysis of the samples collected during the first several sampling intervals (121004, 130109, 130212-130307, 130514-130617, 131105-131106, 140210) and another HPGe (Model: GC2519, SN: 0817390) was used for analysis of the samples collected during the subsequent sampling intervals. Quarterly efficiency calibrations of the germanium detectors were performed using a NIST traceable <sup>152</sup>Eu stock solution. An example calibration curve for sampling event 121004 is shown below (Figure 4.3). As noted on the y-axis, the efficiency varied between 0.5% to 2.5% for the energy range examined. A standard geometry of 200mL of sample in a 250mL wide-mouth polypropylene bottle was used and counted for 24 hours. A quarterly background radiation measurement was made by counting a similar bottle filled with 200 mL of distilled deionized (DDI) water. The background count rate and the efficiency for each isotope were used to calculate the MDC. The MDC values are listed in Table 4.1.



Figure 4-3: HPGe Efficiency curve determined from counting 45 mL of a <sup>152</sup>Eu standard in a 50 mL conical centrifuge tube.

#### Determination of Activity

The list of gamma decay energies and associated intensities used to determine the activities of  ${}^{60}$ Co,  ${}^{137}$ Cs,  ${}^{133}$ Ba, and  ${}^{152}$ Eu are shown in Table 4.2 (National Nuclear Data Center, 2014). The gamma energies in Table 4.2 were chosen because they were emitted with the highest intensities. The activity of  ${}^{137}$ Cs was determined by the count rate for the 0.662 MeV decay energy. The activities of  ${}^{60}$ Co,  ${}^{133}$ Ba, and  ${}^{152}$ Eu were calculated by taking the average of the activities based on the count rates associated with the gamma energies in Table 4.2. The error for  ${}^{137}$ Cs was calculated using counting statistics assuming a 2 $\sigma$  confidence in the average error associated with the efficiency calibration curve, which was 8%. The error for  ${}^{60}$ Co,  ${}^{133}$ Ba, and  ${}^{152}$ Eu was calculated using the standard deviation of the activity measurements based on the gamma decay energies.

Table 4-2: Gamma decay energies and associated intensities of the gamma emitting radionuclides that were used to calculate the activities of the respective radionuclides.

Padionuclida	Gamma Decay	Intensity	
Radionucitue	Energy (MeV)	(unitless)	
<sup>137</sup> Cs	0.662	0.851	
60 <b>C</b> a	1.173	0.999	
	1.332	0.999	
	0.081	0.329	
<sup>133</sup> Ba	0.303	0.183	
	0.356	0.621	
	0.411	0.022	
<sup>152</sup> Eu	0.778	0.129	
	1.089	0.017	

Analysis of the actinides (<sup>237</sup>Np and <sup>239/240</sup>Pu)

Analysis of samples containing <sup>237</sup>Np and <sup>239/240</sup>Pu was performed using a Thermo Scientific ICP-MS (Model: X-2, SN: 012990). Approximately 10 mL of acidified sample was removed from the collection bottles and placed in a 15mL centrifuge tube and subsequently analyzed on the ICP-MS. <sup>237</sup>Np and <sup>239</sup>Pu concentration standards were prepared by diluting NIST standard reference materials 4341 and 4330C for <sup>237</sup>Np and <sup>239</sup>Pu, respectively. The samples were run using <sup>242</sup>Pu as an internal standard to account for changes in flow rate and any changes in sensitivity due to external factors such as fluctuations in temperature, pressure, or humidity. The minimum detectable concentrations for <sup>237</sup>Np and <sup>239</sup>Pu are based on the intercept concentrations of the calibration curves and are shown in Table 4.1 for each of the sampling events.

### Selected Major Ion Concentrations

In addition to the determination of radionuclide concentrations, the concentrations of selected major ions were determined for all sampling events and can be found in the database accompanying this report. The concentrations were determined using ICP-MS. Calibration standards were prepared by diluting NIST traceable multiple element standards. The ions monitored in the effluents from the first three sampling events were potassium (K), magnesium (Mg), iron (Fe), zinc (Zn), and manganese (Mn). Due to the availability of calibration standards, the ions monitored in the effluents from the subsequent sampling events were sodium (Na), Mg, K, calcium (Ca), Mn, and Fe. The concentrations of these elements were quantified to provide estimates of ionic strength of the effluent solutions and to determine the potential for competition between these major ions and the radionuclides of interest.

# Low-level <sup>239/240</sup>Pu measurements

The detection limit for <sup>239</sup>Pu using ICP-MS is approximately  $1 \times 10^{-12}$  M. A second analytical technique was used for select effluent samples to quantify lower concentrations of Pu. This technique, which combines a co–precipitation step with <sup>239/240</sup>Pu detection by alpha spectroscopy, provides a detection limit of ~10<sup>-15</sup> M for <sup>239/240</sup>Pu. First, and after acidification with HNO<sub>3</sub>, 2 mL of a <sup>242</sup>Pu tracer (0.038 Bq/ml, 0.076 Bq total added) was added to select effluent samples. Then, an Fe<sup>III</sup> solution (as FeCl<sub>3</sub>, 10 mg Fe mL<sup>-1</sup>) was added to give an Fe concentration of 200 mg L<sup>-1</sup> in each effluent. Then, concentrated NH<sub>4</sub>OH was added to adjust the pH to ~7, driving co-precipitation of Pu with Fe(OH)<sub>3</sub>. After allowing the precipitate to settle overnight, the amended effluent samples were centrifuged at 4000 rpm for 30 minutes (model: Allegra X-22R, Beckman Coulter). The supernatant was then discarded and the solid was washed with dilute NH<sub>4</sub>OH and then dried overnight. After drying, the precipitate was dissolved in 5 mL of concentrated HNO<sub>3</sub> and diluted with DDI water to give ~3 M HNO<sub>3</sub>. Then a sufficient amount of a solid NaNO<sub>2</sub> was added to give a solution of ~0.025 M NaNO<sub>2</sub>–3 M HNO<sub>3</sub>.

The Pu was extracted from the resulting HNO<sub>3</sub>-NaNO<sub>2</sub> solution using TEVA extraction chromatography resin. TEVA columns were prepared by adding 1 mL of the resin in a 2 ml column (Poly-prep chromatography columns, Bio-Rad). When gravity flow was not sufficient, a vacuum extraction system was used to control the flow rate. The column was first rinsed with 5 column volumes of 0.025 M NaNO<sub>2</sub>–3 M HNO<sub>3</sub>. Then the sample solution was loaded onto the TEVA column. After the sample was loaded, the column was rinsed with 15 mL of 0.025 M NaNO<sub>2</sub>–3 M HNO<sub>3</sub>. To elute plutonium from TEVA resin, 5 column volumes of 0.01 M hydrochloric acid – 0.2M HF were used.

For samples analyzed from 2015 and 2016, the Pu-bearing eluant was evaporated to dryness and then dissolved with concentrated HNO<sub>3</sub> and 30% H<sub>2</sub>O<sub>2</sub> and fumed three times to destroy organic compounds. Afterwards, the sample was dissolved in 0.3 mL concentrated H<sub>2</sub>SO<sub>4</sub> and diluted to 0.5 M H<sub>2</sub>SO<sub>4</sub> by adding DDI water. Then, the pH was adjusted to ~3.2–3.5 by adding small amounts of 10 M NaOH, using a methyl yellow pH indicator to verify that the optimal pH was reached. Pu in the solutions was then electroplated onto steel planchets for 2 h using currents of 0.5 mA per sample, after which the <sup>239/240</sup>Pu activity in each sample was determined using an ~4 day count on an Alpha Spectrometer (EG&G Ortec, Octete PC). The efficiency calibration of the detectors was performed using a NIST traceable electroplated alpha emitting radionuclide standard (<sup>235</sup>U, <sup>238</sup>U, <sup>239</sup>Pu, and <sup>241</sup>Am), giving an efficiency of ~0.07. The background count rate and the

efficiency for each isotope were used to calculate the MDC using equation 1. The error for <sup>239,240</sup>Pu was calculated from counting statistics.

For samples analyzed in 2019 and 2020, the Pu effluent from the column separations described above were prepared for alpha spectroscopy by production of sources using cerium fluoride microprecipitation. Briefly, the effluent was mixed with 50 mg of cerium from a cerium nitrate carrier and then 1 mL of concentrated hydrofluoric acid. The solutions were mixed and then filtered after a 30 minute delay. Eichrom resolve filters were used and washed with an 80% ethanol solution prior to filtration and after filtration to remove residual reagent. The filters were dried under a heat lamp and then attached to stainless steel planchets with adhesive. Samples were analyzed and evaluated as described above.

### 5. RESULTS - GAMMA ISOTOPE LYSIMETERS

#### General Description of Geochemistry

The radioactive constituents contained in the salt waste, <sup>60</sup>Co, <sup>137</sup>Cs, <sup>133</sup>Ba, and <sup>152</sup>Eu, were chosen for this work in order to examine monovalent (<sup>137</sup>Cs), divalent (<sup>60</sup>Co and <sup>133</sup>Ba) and trivalent (<sup>152</sup>Eu) cation release from the saltstone. Cobalt-60 (<sup>60</sup>Co), was chosen for this study as a model fission product as well as commonly being a divalent cation. In terrestrial environments, aqueous <sup>60</sup>Co is found in the Co<sup>II</sup> and Co<sup>III</sup> oxidation states with Co<sup>II</sup> being the dominant state (Collins and Kinsela, 2010). Cobalt mobility in soil is dependent on pH with approximately an order of magnitude variation in  $K_d$  values for one unit change of pH in the soil. Due to its low solubility, Co<sup>III</sup> will only be present in aqueous solutions if complexed with a strong chelating agent (Duckworth et al., 2009). Studies of <sup>60</sup>Co speciation in groundwater as a result of contamination from nuclear waste repositories have shown that when deposited with a strong chelating agent (i.e., ethylenediaminetetraacetic acid [EDTA]), anionic EDTA complexes dominate <sup>60</sup>Co speciation (Caron and Mankarios, 2004; Robertson et al., 1995). Oxidation of Co<sup>II</sup>-EDTA complexes is most likely due to solid phase Fe<sup>III</sup> oxyhydroxides and Mn<sup>IV</sup> oxides (Collins and Kinsela, 2010).

#### Historical and Current Inventory

This study will also provide data that are relevant to performance assessment models at SRS examining reducing grout-based waste forms. SRS currently contains approximately 100 million liters of radioactive waste in 51 underground storage tanks, 43 of which are still operational. The waste in these tanks is in two forms: an insoluble mixture of metal hydroxides and a soluble salt. The soluble salt form makes up 93% of the total waste volume. Treatment of the salt waste is performed by solidifying the waste in a solid form called saltstone. Saltstone is a mix of Portland cement, fly ash, and blast furnace slag, which serves as a reducing agent.

The saltstone sources in this work are composed of a 45:45:10 premixture ratio of fly ash, slag, and cement, respectively (Roberts et al., 2012). Roberts and Kaplan (2009) used the methods described by Angus and Glasser (1985) to measure the reduction capacity of the slag component, which is used to estimate the saltstone reduction capacity. The reported value of 819  $\mu$ eq g<sup>-1</sup> is consistent with values determined in similar studies (Kaplan et al. 2009; Lukens et al. 2005). Lysimeters 16-18 contain saltstone sources amended with a suite of gamma emitting radionuclides, specifically, <sup>60</sup>Co, <sup>137</sup>Cs, <sup>133</sup>Ba, and <sup>152</sup>Eu. Lysimeters 4-6 contain cement sources (a mixture of fly ash and cement with no slag present) amended with the same suite of gamma emitters.

#### Radionuclide Effluent Concentrations

The pH and dissolved oxygen measurements for each lysimeter sampling event are provided in Appendix B. The pH values were generally near pH 5-6 which is consistent with the measured pH of the soil and dissolved oxygen concentrations were near saturation (~8 mg/L).

Nine lysimeters (4–6, 16–18, and 26–28) contained sources with the gamma emitting radionuclides <sup>60</sup>Co, <sup>137</sup>Cs, <sup>133</sup>Ba, and <sup>152</sup>Eu. Theses radionuclides were contained

within a cement matrix without blast furnace slag (BFS) for lysimeters 4-6, within a saltstone matrix with BFS for lysimeters 16–18, and on a filter paper for the control lysimeters 26–28. Of these radionuclides, the effluent concentrations of <sup>60</sup>Co were most regularly the highest and most consistently above the detection limits. Concentration (Bq  $L^{-1}$ ) of <sup>60</sup>Co from each lysimeter containing the suite of gamma emitting radionuclides for each sampling interval is shown in Figure 5-2 alongside the cumulative activities released in each set of lysimeters. For clarity, the plots are grouped by data for individual sets (cement, saltstone, and sediment) and the activities for each lysimeter, by sampling event, are provided in the RadFLEx database. The concentration of <sup>60</sup>Co was greatest in the effluents of lysimeters 4, 5, and 6, which had cumulative releases of 5188, 8964, and 3301 Bq, respectively. Although these concentrations of  $^{60}$ Co are measurable, they still represent a relatively small fraction of the total <sup>60</sup>Co in the source, as discussed below. In almost all cases, the concentrations of <sup>137</sup>Cs, <sup>152</sup>Eu, and <sup>133</sup>Ba were at or below the minimum detectable concentration. Thus, it appears that only a small fraction of <sup>60</sup>Co is mobile in these lysimeters. However, detailed analysis of the solid phase distribution of <sup>60</sup>Co and the other gamma emitting radionuclides is needed to verify this.
				Uncapped -				Lysimeter sectioned		Uncapped -
		Activity	Source	start of	Start interruption of	Ended interruption of	Lysimeter	and	Source	start of
Lys.	Description	(kBq)	emplaced	infiltration	expt	expt	removed	analyzed	emplaced	infiltration
	Cement Gamma	4662							03/24/2017 shipped Clemson to	
4	suite, 2 yr	<sup>15</sup> /Cs;	5/11/2012	7/5/2012	6/13/2013	8/8/2013	10/8/2015		SRNL	4/20/2017
	Cement Gamma	<sup>5106</sup> <sup>60</sup> Co; 3959 <sup>133</sup> Ba:							03/24/2017 shipped Clemson to	
5	suite, 4 yr	0308	5/11/2012	7/5/2012	6/13/2013	8/8/2013	9/8/2016		SRNL	4/20/2017
	Cement Gamma	<sup>152</sup> Eu	- // / /- 0 / -	- / - /						
6	suite, 10 yr		5/11/2012	7/5/2012	6/13/2013	8/8/2013				
	Saltstone Gamma	4662 <sup>137</sup> Cs;							03/24/2017 shipped Clemson to	
16	suite, 2 yr	5106	4/27/2012	7/5/2012	6/13/2013	8/8/2013	9/8/2016		SRNL	4/20/2017
17	Saltstone Gamma suite 4 yr	<sup>60</sup> Co; 3959 <sup>133</sup> Ba	4/27/2012	7/5/2012	6/13/2013	8/8/2013				
17	Saltstone	9398	-1/2//2012	115/2012	0/15/2015	0/0/2015				
	Gamma	<sup>152</sup> Eu								
18	suite, 10 yr		4/27/2012	7/5/2012	6/13/2013	8/8/2013				
26	Gamma suite, 2 yr	292 <sup>137</sup> Cs;	4/27/2012	7/5/2012	6/13/2013	8/8/2013	9/8/2016	SRNL		
	Gamma	318								
27	suite, 4 yr	<sup>60</sup> Co;	4/27/2012	7/5/2012	6/13/2013	8/8/2013				
	Commo	248 <sup>133</sup> Ba;								
28	suite, 10 yr	<sup>152</sup> Eu	4/27/2012	7/5/2012	6/13/2013	8/8/2013				

# Table 5-1: Timeline of gamma lysimeter deployment and inventory in plots.



Figure 5-1: Measured activity concentrations (Bq L<sup>-1</sup>) of <sup>60</sup>Co in the effluent of the cement source-bearing, saltstone, and filter paper lysimeters for each sampling event (respectively, on left). Cumulative activities from the effluent are shown on the right for lysimeters of each source type. Note: samples were not received for the 150106 event.

There are several important observations from this data. First, breakthrough of <sup>60</sup>Co from the lysimeters containing the suite of gamma emitters in cement sources without BFS was approximately an order of magnitude greater than breakthrough from the lysimeters containing the same suite of radionuclides in saltstone sources. Furthermore, the breakthrough of <sup>60</sup>Co from the sediment sources was consistently lower than that from the saltstone and cement sources. However, note that the total activity in

the sediment sources was approximately 16x lower than the saltstone or cement sources. Thus, it appears that the mobilization of  $^{60}$ Co follows the trend:

Cement (no BFS) sources > Saltstone sources > sediment/filter paper This trend is demonstrated from the compiled data in Table 5-2, which lists the  $^{60}$ Co activity released from each lysimeter along with the total  $^{60}$ Co contained in the source. Although the average percent of  $^{60}$ Co released (0.04%) is very low for all sources and the standard deviation of the three replicate lysimeters for each source is high relative to the average, it is clear that the lysimeters containing cement sources without BFS have the highest release of  $^{60}$ Co.

Table 5-2: Cobalt–60 activity released from lysimeters containing saltstone, cement, and sediment sources. Note: The <sup>60</sup>Co detection limit varied slightly between measurement intervals and an average value of 3.8 Bq/L was used to determine concentrations and cumulative activity.

Lysimeter	Source	Cumulative Effluent Volume (mL)	Total activity in source (kBq)	Cumulative activity released in effluent (kBq)
4	Cement	21472	5106	5.20
5	Cement	22,863	5106	8.96
6	Cement	10,384	5106	3.30
16	Saltstone	24,451	5106	0.54
17	Saltstone	14,012	5106	0.74
18	Saltstone	13,357	5106	1.05
26	Soil	11,022	318	0, BLD
27	Soil	34,124	318	1.9 x 10 <sup>-3</sup>
28	Soil	32,393	318	8.1 x 10 <sup>-3</sup>

The main factor controlling the variability of radionuclide breakthrough for the cement and saltstone lysimeters containing the gamma–emitting radionuclide suite is the cumulative effluent volume collected. There is approximately 10 L difference between the maximum and minimum effluent collected in each set of cement/saltstone bearing

lysimeters. This variability may also be an indication that the cementitious sources are aging differently. The existence of large pores, fracturing, or cracking occurring as the cement and saltstone sources age and interact with the surrounding soil under variable soil moisture conditions could enhance water infiltration into the interior of the source, thereby promoting radionuclide leaching. The variability may also be an indication of compromises in the integrity of the source, which will be investigated once the lysimeters are removed.

Another important observation made from this data is that the release of <sup>60</sup>Co from lysimeters 26–28 was negligible. These three lysimeters have sources in which the suite of gamma–emitting radionuclides was directly added to a filter paper. Because these radionuclides were not contained within cement or saltstone, it was expected that greater breakthrough would occur, relative to the lysimeters containing cement or saltstone gamma–emitting radionuclides. However, the data indicate that the cement and saltstone enhance the transport of Co, but it is unclear why this is the case. It will be beneficial to examine both the source and soil column from each of the sets of gamma suite containing lysimeters in order to determine whether there has been release from the source of any of the other radionuclides, and if there has been any fracturing in the source that has facilitated release from the source and subsequent transport.

The breakthrough from the lysimeters containing the suite of gamma emitting radionuclides can be conceptualized using knowledge of the geochemical interactions controlling transport of each radionuclide. One approach for predicting this breakthrough is to use partition coefficients ( $K_d$ ).  $K_d$  is an important parameter that defines the

partitioning of an analyte between solid and aqueous phases and therefore represents a measure of retarded mobility. Examining the  $K_d$  values and controlling surficial interactions of the gamma emitting radionuclides included in the RadFLEx study can help explain the observations in this discussion.

The mobility of monovalent Cs is controlled by sorption and cation exchange with clay minerals in soil (Giannakopoulou et al., 2007). Metal concentration, pH, ionic strength, and temperature influence these interactions (Giannakopoulou et al., 2007). Previous explanation of the valence state and sorption behavior of Co at relevant conditions should be considered in this discussion. Additionally, the partitioning of Co varies with pH, redox conditions, ionic strength and dissolved organic matter content, with sorption to iron and manganese oxides and clay minerals limiting mobility (Kim et al., 2006; Krupka and Serne, 2002). The mobility of Ba is controlled by 1) sorption based on the cation exchange capacity (CEC) of the soil and 2) the solubility of Ba particularly in the presence of sulfate and carbonate which can form insoluble BaSO<sub>4</sub>(s) and BaCO<sub>3</sub>(s) phases. Adsorption of Ba, facilitated through the incorporation in clay minerals, will increase with increased soil CEC (Medejon, 2012). Precipitation as witherite (BaCO<sub>3</sub>) will also limit mobility in the presence of elevated CaCO<sub>3</sub> content. Sulfate concentrations will also control Ba mobility due to the formation of the BaSO<sub>4</sub>, which has a very low solubility. The high sorption affinity (and high  $K_d$ ) of trivalent Eu to sediment is likely due to its low solubility in natural environments (Krupka and Serne, 2002).

 $K_d$  values for the gamma-emitting radionuclides are listed in Table 5-3. In the work by Grogan et al. (2010), Cs and Co sorption experiments were performed with sediment from the upper and lower valoes zone, and aquifer zone at the E-Area of the SRS. The values listed in the table are the  $K_d$  values calculated from Cs and Co sorption to the lower valoes zone sediment because the soil characteristics of this zone are most representative of the soil used in the RadFLEx experiments. The  $K_d$  value listed for Eu was determined from a study of Eu sorption to a clayey soil from the SRS (Kaplan et al., 2010b). A Ba  $K_d$  range of 5 to 50 L/kg was reported by Seaman and Chang (2013) when examining Ba sorption to two SRS end-member soils and a soil from the Saltstone Disposal Facility. This range is similar to the value of 80 L/kg reported by Miller (2010) based on a linear extrapolation between measured sorption distribution coefficients of Sr and Ra. Similar to Ba, Ra and Sr are divalent cations and as shown in Sposito (1989), the sorption affinity for alkaline earth metals will follow the trend of increasing sorption with increasing ionic radii ( $Ra^{2+} > Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ ).

Interestingly, breakthrough from the lysimeters containing the suite of gamma– emitting radionuclides is not consistent with the K<sub>d</sub> values listed in Table 5-3. We would expect mobility of the radionuclides to increase with decreasing K<sub>d</sub> values. However, only breakthrough of Co has been observed thus far, even though Ba has a similar K<sub>d</sub> value, and Cs has a much smaller sorption K<sub>d</sub> value. It would be expected, based on these values, that Cs breakthrough should have occurred first or at least in greater quantities than Co. However, work performed in FY19 demonstrated that Kd values determined from desorption studies of soils where <sup>137</sup>Cs had equilibrated with soils for longer time periods yielded much higher K<sub>d</sub> values (right hand column, Table 5-3). This indicates there is an "aging" process by which <sup>137</sup>Cs attenuation by the soil increases with time, consistent with several recent studies (Goto et al., 2014; Barber, 2017; Seigler, 2019). Investigations of the soil columns from these lysimeters may provide further information on this potential aging process.

Radionuclide	Sorption Determined K <sub>d</sub> , L kg <sup>-1</sup>	Desorption K <sub>d</sub> , L kg <sup>-1</sup> (Stdev) measured from Lysimeter 26 Soils (Coutelot et al., 2020)
<sup>137</sup> Cs	6 (Grogan et al., 2010)	2242 (375)
<sup>60</sup> Co	58 (Grogan et al., 2010)	29 (9)
<sup>152</sup> Eu	9,021 (Kaplan et al., 2010b)	4293 (2896)
<sup>133</sup> Ba	Range 5 to 50*	28.5 (3.7)

Table 5-3: Sediment:water partition coefficient (K<sub>d</sub>) values for the radionuclides in the lysimeters containing the suite of gamma-emitting radionuclides.

\*Range of reported values examining sorption to sand and clay end-member soils and a soil from the Saltstone Disposal Facility.

### 6. RESULTS - NEPTUNIUM LYSIMETERS

#### General Description of Geochemistry

Due to its long half-life (2.14 x  $10^6$  years) and its relatively fast mobility in the subsurface, the contribution of neptunium (Np) to the radioactivity inventory in nuclear waste repositories is an important consideration. Both Np<sup>IV</sup> and Np<sup>V</sup> oxidation states may exist in the environment. However, in mildly oxic aqueous conditions, Np<sup>V</sup> is the dominant species (Kaszuba and Runde, 1999), thus we expect predominantly Np<sup>V</sup> in the RadFLEx experiments. The high solubility of the Np<sup>V</sup> solid phases and weak sorption of Np<sup>V</sup> make it very mobile under most environmental conditions. Tetravalent neptunium is more commonly found under highly reducing conditions and is far less mobile due to its lower solubility and greater tendency to form surface complexes (Kaszuba and Runde, 1999).

Previous work examining sorption of Np<sup>V</sup> to SRS soil (Miller, 2010) demonstrated that sorption is completely reversible, thus allowing simulation using either  $K_d$  values or surface complexation models. Additional sorption experiments in the presence of NOM and other reducing agents, that would promote competition for sorption, had little effect on sorption behavior. The sorption data was modeled using a diffuse-double layer model and calibrated using an iron concentration and site density estimated based on the citrate-bicarbonate-dithionite (CDB) extractable iron content. It was determined that 4% of the soil Fe was reactive with Np. The sorption data were modeled using 1:1 (pH values less than 7) and both 1:1 and 2:1 (pH values greater than 7) Np: FeOH surface complexes, which reacted with the 4% of reactive iron content in the soil (Miller, 2010). These findings can be exploited for modeling Np transport in the RadFLEx study because only the aforementioned surface complexes need to be considered.

The pH and dissolved oxygen measurements for each lysimeter sampling event are provided in Appendix B. The pH values were generally near pH 5-6 which is consistent with the measured pH of the soil and dissolved oxygen concentrations were near saturation (~8 mg/L).

### Historical and Current Inventory

There are lysimeters containing  $Np^{IV}$  and  $Np^{V}$  sources that can be used as oxidation state chemical analogs of plutonium.

Lys.	Description	Source emplaced	Uncapped - start of infiltration	Start interuption of expt	Ended interuption of expt	Lysimeter removed	Source emplaced	Uncapped - start of infiltration
8-2	Np(IV)O <sub>2</sub>						10/24/19	10/24/19
29	Np(V)- nitrate, 1 yr	5/11/12	7/5/12	6/13/13	8/8/13	10/8/15		
29-2	Np(IV)O <sub>2</sub>						10/24/19	10/24/19
30	Np(V)- nitrate, 4 yr	5/11/12	7/5/12	6/13/13	8/8/13			
31	Np(IV)O <sub>2</sub> , 4 yr	5/11/12	7/5/12	6/13/13	8/8/13	10/8/15		
31-2	Np(V)- nitrate						10/24/19	10/24/19
32	Np(IV)O <sub>2</sub> , 10 yr	5/11/12	7/5/12	6/13/13	8/8/13			
33-2	Np(V)- nitrate						10/24/19	10/24/19

Table 6-1: Timeline of Np lysimeter deployment and port locations.

#### Radionuclide Effluent Concentrations

No measurable release of <sup>237</sup>Np was observed during the first three sampling events from the four neptunium–containing lysimeters (lysimeters 29 - 32; source emplaced on 5/11/2012). Neptunium breakthrough from lysimeters containing Np<sup>V</sup> sources was first observed for the 130307 sampling event, in which lysimeter 30 had a release of 126 Bq, and for the 131106 sampling event, in which lysimeter 29 had a release of 0.97 Bq. Plots of the cumulative activity of Np (in Bq) released as a function of the cumulative volume of water through lysimeters 29 and 30 are shown in Figure 6-1. Although the total activity of Np released from each lysimeter varies, the aqueous concentrations of Np in the effluent from lysimeters 29 and 30 approach a similar value (Figure 6-1). To date, there has been a total of 17,627 Bq released from lysimeter 30 and 1,558 Bq from lysimeter 29 (note lysimeter 29 was removed for destructive sampling 10/8/2015).



Figure 6-1: The breakthrough of <sup>237</sup>Np from lysimeters 29 and 30 containing Np(V) sources shown as the cumulative mass measured in the effluent as a function of cumulative water volume collected. Note that lysimeter 29 was removed and destructively analyzed in 2015.



Figure 6-2: The cumulative <sup>237</sup>Np mass released from lysimeters 31 and 32 containing Np(IV) sources as a function of cumulative water volume collected. Note that lysimeter 31 was removed and destructively analyzed in 2015.

Breakthrough from lysimeters 31 and 32, which contained Np<sup>IV</sup> sources, was not observed until 2014 and has continued for lysimeter 32. Plots of the cumulative mass of Np observed in the effluent as a function of the cumulative volume of water through lysimeters 31 and 32 is shown in Figure 6-2 (note that lysimeter 31 was removed for destructive analysis in 2015). Np breakthrough from lysimeter 32 was confirmed in the 141105 sampling event, with 0.001 ppb Np measured in the effluent (only slightly above the ICPMS detection limit). Almost all effluent samples collected from lysimeter 32 from 2015 to 2020 contained measurable Np release (with the exception of 150326 and 150714), with a cumulative activity of 51 Bq measured as of FY20, an ~9 Bq increase since FY19. Measurable releases of Np from lysimeter 32 continued and remained consistent throughout the sampling events in FY20. The measurement of Np in the effluent of lysimeter 32, which contained a Np<sup>IV</sup> source, is likely due to oxidation of the source material (i.e., Np<sup>IV</sup> to Np<sup>V</sup>) with exposure to pore water over time. However, the steady-state aqueous Np concentration measured in the effluent from lysimeter 32 (Np<sup>IV</sup>O<sub>2</sub> source) is two to four orders of magnitude lower than the concentrations measured in effluent from lysimeters 29 and 30 (Np<sup>V</sup>O<sub>2</sub>NO<sub>3</sub> sources), suggesting that release of Np and transport through the soil is solubility controlled.



Figure 6-3: The breakthrough of <sup>237</sup>Np from lysimeters 32 shown as the cumulative activity measured in the effluent as a function of cumulative water volume collected.



Figure 6-4: Accumulated activity released as a function of cumulative effluent volume. Error bars are included but hidden by some markers, and the error has been propagated for each successive effluent measurement.

The observed mobility from lysimeters 29 and 30 was expected based on the known mobility of Np(V) which will be present as the free ion, NpO<sub>2</sub><sup>+</sup>, under these conditions. In the work by Miller (2010), a K<sub>d</sub> value of 9.05 L kg<sup>-1</sup> was experimentally determined for Np sorption to SRS subsurface soil. Based on this K<sub>d</sub> value and the K<sub>d</sub> values of the gamma emitting radionuclides (Table 5-3) the observed breakthrough of Np was expected. The downward migration of Np is controlled by the wetting and drying periods in the soil, where transport occurs during the wetting period and is temporarily halted during drying. The transport of Np<sup>V</sup> is strongly dependent on pH, and under the conditions in the RadFLEx experiment Np<sup>V</sup> sorption will not be strong enough to further retard Np mobility during the cyclic periods (Miller, 2010). It is noteworthy that

breakthrough from lysimeter 29 occurred after a cumulative volume of 5,465 mL was collected, compared to 2,796 mL collected from lysimeter 30. It is unlikely that there is an additional mechanism retarding the migration of Np in lysimeter 29, which provides further evidence of the variability that inherently exists in these experiments. The difference in the effluent activity between lysimeters 29 and 30 is proposed to be due to a heterogeneous flow field of water through the lysimeter. Additional tracer studies and possibly ex situ imaging (x-ray computed tomography) studies of water movement through the lysimeters are needed to verify the degree of heterogeneity.

Solid phase analysis of lysimeter 29 was performed, showing an average concentration of <sup>237</sup>Np in the soil of 3.42 Bq/g soil (Peruski et al., 2018). No source material remained after 3 years in the lysimeter test bed. Solid phase analysis of lysimeter 30 has not been performed since the lysimeter is still active, but given the significantly higher release of <sup>237</sup>Np in the effluent of lysimeter 30, as compared to lysimeter 29, it may be expected that sediment concentrations would be lower, assuming initially equal activity sources.

The observation of Np in the effluent from lysimeter 32 is an unexpected and interesting finding. The NpO<sub>2</sub>(s) source within lysimeter 32 is an insoluble phase which is expected to have a solubility comparable to that of PuO<sub>2</sub>(s) (i.e.  $\sim 10^{-14}$  M). Therefore, it is likely that some fraction of the NpO<sub>2</sub>(s) phase has become oxidized and Np<sup>V</sup> is leaching from the source. This hypothesis is based on the observation of Np in the effluent far above the expected solubility of NpO<sub>2</sub>(s). This hypothesis was confirmed

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using a combination of scanning electron microscopy and x-ray absorption spectroscopy as described by Peruski et al., (2018).

### 7. RESULTS - PLUTONIUM LYSIMETERS

#### General Description of Geochemistry

Plutonium (Pu) mobility in soil is largely governed by its oxidation state. Plutonium is unique in that it may simultaneously exist as reduced Pu<sup>III/IV</sup> and oxidized Pu<sup>V/VI</sup> in a given system (Cleveland, 1979). Geochemical behavior, such as complexation strength and hydrolysis of Pu increases with increasing effective charge of the ion (Choppin, 1983):

$$\begin{array}{rll} Pu^{4+} &> & Pu^{VI}O_2{}^{2+} > Pu^{3+} > Pu^{V}O_2{}^{+} \\ +4.0 & +3.2 & +3.0 & +2.2 \end{array}$$

The increased effective charge of the plutonyl (i.e.  $Pu^{V}$  and  $Pu^{VI}$ ) oxidation states is due to the axial oxygen atoms (Kim, 1986). Far field transport of Pu has also been facilitated by the presence of colloids with kilometer scale transport observed at the Nevada Test Site (Kersting et al., 1999). Previous lysimeter experiments of Pu transport in SRS soils have shown the importance of the oxidation state of the source and oxidation and reduction reactions on Pu mobility (Kaplan et al., 2004, 2006a, 2006b). An 11-year field lysimeter study by Kaplan et al. (2004) employed four lysimeters containing three reduced sources (one  $Pu^{III}$  and two  $Pu^{IV}$ ) and one oxidized source ( $Pu^{VI}$ ). The main finding was that in each lysimeter, 95% of the Pu was found within 1.25 cm from the source. Reactive transport modeling and oxidation state analysis of the Pu within the soil showed that >90% was present as the immobile  $Pu^{IV}$  (Kaplan et al., 2004; Kaplan et al., 2006a). Decreasing concentrations of Pu with depth were found in the reduced Pu lysimeters as far as 40 cm from the surface. It is evident that in these lysimeters Pu underwent cyclic oxidation and reduction. This conceptual model is consistent with the wetting and drying cycles within the lysimeter soil profile where penetrating water will cause Pu oxidation and subsequent downward movement. Drying will then cause Pu reduction to the immobile Pu<sup>IV</sup> state.

The RadFLEx facility includes initially contained18 lysimeters (Table 7-1) bearing Pu sources in the III, IV, and V oxidation states. The varying oxidation states were used to test the conceptual models with regards to the mobility of Pu under varying oxidation states discussed above. Additional modifications were made as discussed below to examine the influence of organic matter and/or plant uptake.

Lysimeters 9, 10, and 11 were amended with grass in order to observe the effect of vegetation on Pu transport. The addition of vegetation was made because upward migration of Pu, attributed to plant root uptake, was observed in the previous lysimeter studies (Demirkanli et al., 2009, Kaplan et al., 2010, Molz et al., 2014). Experimental data and agreement with models suggest that naturalized grass grown on the previous lysimeters was responsible for transport up in the root xylem and into the above-ground parts of the plant. This would result in Pu deposition on the surface of the lysimeter during die-back with any remaining Pu in the roots diffusing back into the soil. The rate of uptake in the grass roots is 5 x  $10^6$  times faster than in corn (Molz et al., 2014), which likely contributed to the majority of the Pu concentration measured above the source in previous lysimeter studies (Kaplan et al., 2004; Kaplan et al., 2006a). Another possible contribution to the upward migration is a vertical soil water flow to roots that is not a parameter in current 1-D modeling approaches, such as microbial chemotaxis (Molz et al., 2012).

al., 2014). The set of lysimeters with well characterized sources that have been amended with Bahia grass will be useful in validating previous concepts and conjectures. The breadth of the sources and amendments of the Pu lysimeters will increase the understanding of Pu mobility through sediment gained from the previous studies, though the results from those studies suggest that little to no Pu breakthrough will occur for the planned duration of the RadFLEx experiments.

Initially deployed lysimeters 21, 22, and 23 were amended with organic matter to evaluate the potential for Pu-organic matter complexes to impact plutonium migration (Roberts et al., 2012; Conroy et al., 2017; Maloubier et al., 2020). The sorption capacity and solubility of Pu<sup>IV</sup> is strongly influenced by NOM due to the formation of Pu-NOM complexes (Santschi et al., 2002; Zimmerman et al., 2014). Santchi et al., (2002) demonstrated that natural organic matter may increase Pu mobility. A comparable decrease in sorption of plutonium to goethite was observed by Conroy et al., (2017) but only under elevated pH conditions. Under low pH conditions, Conroy et al., (2017) observed increased sorption of plutonium, presumably due to the formation of ternary surface complexes where organic matter was coating the mineral surfaces. In 2014, Lysimeters 21 and 41 were removed for destructive sampling. Both lysimeters contained  $NH_4PuO_2CO_3(s)$  sources but lysimeter 21 was amended with organic matter. The data revealed two noteworthy observations: 1) Pu downward migration was retarded in the presence of natural organic matter and 2) reduction of the initial Pu(V) source to a Pu(IV)O<sub>2</sub>-type phase was faster in the presence of natural organic matter. Thus, it is unclear if the retardation of Pu migration was due to formation of ternary Pu-organic

matter surface complexes as identified by Conroy et al., (2017) or due to reduction of mobile Pu(V) to relatively immobile Pu(IV). To examine these systems further, several new Pu bearing lysimeters amended with organic matter were added to RadFLEx in 2019 (lysimeters 14-2, 20-2, and 21-3 listed in Table 7-1.

Lys.	Description	Source emplaced	Uncapped - start of infiltration	Start interruption of expt	Ended interruption of expt	Lysimeter removed	Lysimeter sectioned and analyzed	Source emplaced	Uncapped - start of infiltration
9*	Pu(IV)-oxalate, Grass, 2 yr	6/20/2012	7/5/2012	6/13/2013	8/8/2013	10/16/2014*			
10	Pu(IV)-oxalate, Grass, 4 yr	6/20/2012	7/5/2012	6/13/2013	8/8/2013				
11	Pu(IV)-oxalate, Grass, 10 yr	6/20/2012	7/5/2012	6/13/2013	8/8/2013				
13-2*	Pu(IV)-oxalate, Grass, 2 yr							10/16/2014*	10/16/2014*
14-2	Pu(V)NH4CO3/OM							10/24/2019	10/24/2019
20-2	Pu(V)NH4CO3/OM							10/24/2019	10/24/2019
21	Pu(V)NH4 (CO3)/OM, 2 yr	6/20/2012	7/5/2012	6/13/2013	8/8/2013	10/16/2014			
21-3	Pu(V)NH4CO3/OM							10/24/2019	10/24/2019
22	Pu(V)NH4 (CO3)/OM, 4 yr	6/20/2012	7/5/2012	6/13/2013	8/8/2013				
23	Pu(V)NH4 (CO3)/OM, 10 yr	6/20/2012	7/5/2012	6/13/2013	8/8/2013				
33	Pu(III)-oxalate, 2 yr	6/20/2012	7/5/2012	6/13/2013	8/8/2013	10/8/2015	Clemson		
34	Pu(III)-oxalate, 4 yr	6/20/2012	7/5/2012	6/13/2013	8/8/2013				
35	Pu(III)-oxalate, 10 yr	6/20/2012	7/5/2012	6/13/2013	8/8/2013				
38	Pu(IV)-oxalate, 2 yr	6/20/2012	7/5/2012	6/13/2013	8/8/2013	10/8/2015	Clemson		
38-3	Pu(V)NH4(CO3)/sand, 2 yr							10/24/2019	10/24/2019
39	Pu(IV)-oxalate, 4 yr	6/20/2012	7/5/2012	6/13/2013	8/8/2013				
40	Pu(IV)-oxalate, 10 yr	6/20/2012	7/5/2012	6/13/2013	8/8/2013				
41	Pu(V)NH4 (CO3), 2 yr	6/20/2012	7/5/2012	6/13/2013	8/8/2013	10/16/2014			
41-3	Pu(V)NH4(CO3)/sand, 4 yr							10/24/2019	10/24/2019
42	Pu(V)NH4 (CO3), 4 yr	6/20/2012	7/5/2012	5/14/2013	8/8/2013				
43	Pu(V)NH4 (CO3), 10 yr	6/20/2012	7/5/2012	5/14/2013	8/8/2013				
44	Pu(IV)O2 colloids, 2 yr	5/11/2012	7/5/2012	5/14/2013	8/8/2013	10/8/2015	Clemson		
44-3	Pu(V)NH4(CO3)/sand, 10 yr							10/24/2019	10/24/2019
45	Pu(IV)O2 colloids, 4 yr	5/11/2012	7/5/2012	5/14/2013	8/8/2013				
46	Pu(IV)O2 colloids, 10 yr	5/11/2012	7/5/2012	6/13/2013	8/8/2013				

## Table 7-1: Listing of deployment and sampling of Pu bearing RadFLEx lysimeters

\*Lysimeter 9 was moved to slot 13 at the RadFLEx facility on 10/16/2014

### Dissolved Oxygen, pH, and Pu Concentrations

In FY20, Lysimeters 14-2, 20-2, and 21-3 contained less dissolved oxygen than the expected averages (Table 7-2). Dissolved oxygen measurements are often near the oxygen solubility limit for water in most samples (~8 mg/L), as the samples are not preserved before receipt for analysis. However, Lysimeters 14-2, 20-2, and 21-3 each produced brown, turbid effluents that required filtration before analysis on the ICPMS, and the measurements for dissolved oxygen were 1.2, 0.0, 0.1, and 4.5 mg/L (200122-20-S, 200122-21-S, 200311-14-S, and 200311-20-S, respectively). These measurements also corresponded to the observation of plutonium at ppb levels in the effluent (Table 7-2). It is noteworthy that the pH of these effluents were also higher than most other lysimeters and ranged from 7.16 to 7.56. These are new deployments of OM-amended Pu lysimeters, and the associated breakthroughs of Pu indicate a relationship between consumption of oxygen (likely producing a near-reducing environment in the soil), OM content, and Pu mobility. During FY21, further analysis will be performed on these lysimeters since breakthrough has occurred so swiftly.

Table 7-2: Measured dissolved oxygen and plutonium concentrations in lysimeter 14-2,20-2, and 21-3.

	Sampling	g Event 20012	2	Sampling Event 200311			
Lysimeter	Pu	Pu Dissolved		Pu	Dissolved		
Lysinicter	Concentration	Oxygen		Concentration	Oxygen		
	(mol/L)	(mg/L)	pН	(mol/L)	(mg/L)	pН	
14-2	NA	NA	NA	2.2 x 10 <sup>-11</sup>	0.1	7.34	
20-2	8.6 x 10 <sup>-11</sup>	1.2	7.16	4.3 x 10 <sup>-12</sup>	4.5	7.56	
21-3	2.2 x 10 <sup>-11</sup>	0.0	7.03	NA	NA	NA	

#### Low-level Plutonium Analysis

To date, analysis via ICP–MS (detection limit of  $\sim 1 \times 10^{-12}$  M for <sup>239</sup>Pu) has indicated no measurable release of <sup>239</sup>Pu from the eighteen lysimeters containing plutonium that were installed in 2012 (i.e., Lysimeters 9 – 11, 21 – 23, 33 – 35, and 38 – 46). A coprecipitation technique coupled with alpha spectroscopy, which concentrates Pu from larger volumes, was also used to quantify <sup>239</sup>Pu in select effluent samples (sampling events 150326, 151216, and 160301) at concentrations below the ICP–MS detection limit. These additional measurements were completed for effluent samples with volumes greater than 1 L and for the same lysimeter, when possible, to evaluate changes in effluent Pu concentration as a function of time.

In 2016, a total of 17 effluent samples from sampling events 150326, 151216 and 160301, were analyzed and reported in the FY17 report with concentrations between  $9 \times 10^{-13}$  M and  $10^{-15}$  M with detection limits of  $1-5 \times 10^{-15}$  mol/L and uncertainties ranging from 10–20%, depending on the alpha spectrometer used. The measured values were previously reported and are shown in Table 7-3 to provide a complete record in this report.

Sampling Event	15	0326	151216/1	51008	160301	
Lysimeter	Measured Pu (M)	Uncertainty (M)	Measured Pu (M)	Uncertainty (M)	Measured Pu (M)	Uncertainty (M)
11	8 x 10 <sup>-15</sup>	1 x 10 <sup>-15</sup>	$< 5 \ge 10^{-15}$		$< 5 \ge 10^{-15}$	
33	9 x 10 <sup>-13</sup>	2 x 10 <sup>-13</sup>	< 1.1 x 10 <sup>-14</sup>			
35			8.6 x 10 <sup>-15</sup>	1 x 10 <sup>-15</sup>		
39	3.8 x 10 <sup>-13</sup>	5 x 10 <sup>-14</sup>				
45			2.6 x 10 <sup>-14</sup>	4 x 10 <sup>-15</sup>	1.6 x 10 <sup>-14</sup>	2 x 10 <sup>-15</sup>
46	9 x 10 <sup>-13</sup>	2 x 10 <sup>-13</sup>				

 Table 7-3: <sup>239/240</sup>Pu concentration in effluent from Pu bearing lysimeters at three sampling intervals.

In 2019, twelve samples from the 190716 sampling event were analyzed using the same low-level procedure utilizing coprecipitation and alpha spectroscopy. Of the 12 samples analyzed, only 6 contained <sup>239/240</sup>Pu concentrations above the detection limit (Table 7-4). For reference, the ICPMS detection limit is approximately 4 x 10<sup>-12</sup> mol/L while the minimum detection using alpha spectroscopy is approximately 10<sup>-15</sup> mol/L (Note the detection limit varies with the initial volume of the sample which varies for the lysimeter effluents). Lysimeters 11, 35, 39, and 46 have data for both the 2016 analysis (sampling events 150326, 151216 and 160301) and the 2019 analysis (190716 sampling event). For all four of these lysimeters, higher concentrations of <sup>239</sup>Pu were observed in the 2019 samples. The uncertainty on the L46 measurement decreased from 22.2% to 13.5% between the events.

	Concentration		Concentration	Uncertainty
Lysimeter	(g/L)	Uncertainty (g/L)	(M)	(M)
11	3.3 x 10 <sup>-10</sup>	9.1 x 10 <sup>-11</sup>	1.4 x 10 <sup>-12</sup>	3.8 x 10 <sup>-13</sup>
22	1.5 x 10 <sup>-9</sup>	8.3 x 10 <sup>-11</sup>	6.1 x 10 <sup>-12</sup>	3.5 x 10 <sup>-13</sup>
35	3.2 x 10 <sup>-10</sup>	4.5 x 10 <sup>-11</sup>	1.3 x 10 <sup>-12</sup>	1.9 x 10 <sup>-13</sup>
39	9.0 x 10 <sup>-10</sup>	1.0 x 10 <sup>-10</sup>	3.8 x 10 <sup>-12</sup>	4.3 x 10 <sup>-13</sup>
40	5.5 x 10 <sup>-9</sup>	3.3 x 10 <sup>-10</sup>	2.3 x 10 <sup>-11</sup>	1.4 x 10 <sup>-12</sup>
46	2.2 x 10 <sup>-10</sup>	2.9 x 10 <sup>-11</sup>	9.0 x 10 <sup>-13</sup>	1.2 x 10 <sup>-13</sup>
9,10, 23, 42, 43, 45	BLD*	-	BLD*	-

Table 7-4: <sup>239/240</sup>Pu concentration in effluent from Pu bearing lysimeters for the190716 sampling event.

\*Below Detection Limit (BLD) of approximately 10<sup>-15</sup> M

All reported values are at or above detection limits and are near the solubility limits of Pu<sup>IV</sup> hydroxide phases. The uncertainty values are high due to the extremely low concentrations of Pu measured. The solubility of tetravalent plutonium is very complicated due to the potential of aqueous plutonium to oxidize or reduce and due to the formation of Pu(IV) colloids (Neck *et al.*, 2001; Neck *et al.*, 2007). Reported solubility products for crystalline PuO<sub>2</sub>(crys,s) are 10<sup>-64</sup> and for hydrous Pu(IV)O<sub>2</sub>(hyd,s) are 10<sup>-58.5</sup> (Neck *et al.*, 2001). The expected Pu concentrations using these values range from 10<sup>-15</sup> to 10<sup>-11</sup> mol/L and measured values varying by up to 4 orders of magnitude have been observed and attributed to redox reactions and colloidal Pu(IV) (Neck *et al.*, 2007). Though solubility limitations are apparent in the data, these results positively identify <sup>239/240</sup>Pu in the effluent. In desorption experiments using Pu amended soils from a previous set of field lysimeter studies, Kaplan et al., (2006b) observed solubility dependent leaching behavior, consistent with the results presented here. Thus, it appears that small concentrations of mobile Pu are breaking through the lysimeters, though this mass of Pu represents only a small fraction of the total activity in the source. Albeit a labor-intensive process, continuing this method for one lysimeter in each category of source materials could be beneficial to observe a breakthrough curve, since concentrations have been near the solubility limit of Pu(IV) hydroxide phases but have been increasing over the past 4 years.

The observation of extremely low concentrations of aqueous Pu is consistent with a solubility control as previously observed (Kaplan et al., 2006b; Neck and Kim, 2001; Neck et al., 2007). The low concentrations of Pu in the effluent is also consistent with the currently accepted model that plutonium has limited mobility in the subsurface primarily due to reduction of mobile  $Pu^{V}$  to immobile  $Pu^{IV}$  on mineral surfaces (Kaplan et al., 2004). Based on the high K<sub>d</sub> values of  $Pu^{IV}$  in SRS soils, it is expected that mobile  $Pu^{IV}$  is present as the soluble pentavalent  $PuO_2^+$  dioxycation (Powell et al., 2014).

### 8. DATABASE DEVELOPMENT

A major activity of the FY19 effort described in this report was the development of a database containing all data collected to date on this project. The database was developed in Microsoft Excel to allow easy manipulation of the data and a copy of the database is provided with this report. The key aspects of the database include:

- A page listing all relevant metadata for the lysimeters including measured pH, DO, water volume, radionuclide concentrations with associated uncertainty, and major ion concentrations with associated uncertainty.
- 2. A link to the raw datafiles and data processing files used to determine the values reported with the metadata.
- 3. A listing of the analytical or radioanalytical detection limits for each lysimeter effluent sampling event.
- 4. A link to the raw background and detection limit calculations.
- 5. A convenient color coding of the metadata cells to note issues with the sample including: 1) insufficient sample volume for analysis, 2) reported sample concentrations outside a linear calibration range, and 3) samples below the detection limit.
- 6. A log page to describe any modifications to the database along with the date of the modification and the user.
- 7. A verification box for sample receipt and data QA/QC.

The database was further refined in FY20 with the addition of subtabs with each radioisotope of interest and data calling columns that will allow for detailed evaluation of the data for each radionuclide and production of figures from the data. Additionally, new lysimeters deployed in FY19 were added to each of the subtabs.

The file is called RadFLEx\_Compiled\_Database.xls and an electronic copy is provided with this report.

### 9. pH and DISSOLVED OXYGEN MEASUREMENTS

The pH measurements of the lysimeter effluent for sampling events ranged from 3.32–8.31, with a geomean of 5.01 and standard deviation of 0.66 for the latest sampling interval. This geomean pH is near the measured pH of the soil of 5.27, as reported in Table 3-1. Figure 8-1 shows the measured pH values for all sampling events to date for a lysimeter with relatively high variation between sampling dates (Lysimeter 6) and relatively low variation (Lysimeter 27). Furthermore, there were also fluctuations in pH during each of the sampling events, with the highest values observed during the 160301 sampling events which may be due to the shorter sample collection time which did not allow sufficient time for the leachate to reach equilibrium with the soil. Also, several measurements from the 130514-130617 sampling event (lysimeters 4, 5, and 6) appear anomalous with values between pH 3 and 4. However, the effluent from subsequent events is near the average pH of all samples.





Figure 8-1: The measured pH values of the effluent from lysimeters showing relatively high variability (upper figure, lysimeter 6) and relatively consistent pH vales (lower figure, lysimeter 27) for all sampling events to date. Plots of the measured pH versus time are shown in Appendix B for all lysimeters.

The observed variability in the pH measurements is important for the overall understanding of these systems. Each lysimeter was packed with the same soil and was exposed to similar weather conditions (i.e., temperature and relative precipitation volume), yet differences in pH as high as four units were measured. Furthermore, there is no trend in the effluent pH of lysimeters containing cement and saltstone sources (lysimeters 2–8 and 14–20). Portlandite (calcium hydroxide, Ca(OH)<sub>2</sub>) and calcite (calcium carbonate, CaCO<sub>3</sub>) in the cement are expected to leach when in contact with water and increase the pH of the surrounding environment, but no evidence of this mechanism was observed. Qualitatively, the lysimeters containing cement and saltstone sources appear to have greater variability than other lysimeters. Because we expect radionuclide transport to be greatly affected by pH, variability in effluent pH for lysimeters containing the same source material may help to explain any differences in breakthrough. However, it does appear that the geomean pH of the lysimeters is approaching a constant value of approximately pH 5 (see Figure 8-2 and Appendix B). The convergence of the effluent pH to a value of approximately 5 is consistent with the leachate achieving equilibrium with the soil used to pack the lysimeters (Powell et al., 2014; Kaplan et al., 2004).



Figure 8-2: Geomean and standard deviation of measured pH of all lysimeter effluent samples collected during each sampling event.

Less variability, relative to measured pH, was observed in the measured DO content of the lysimeter effluent samples. The DO content of water in equilibrium with air is inversely proportional to temperature, with higher temperatures corresponding to lower DO. To provide the most accurate measurement of DO content and to minimize sample perturbation, DO was measured as quickly as possible upon receipt of the effluent samples. Because no attempt was made during sampling and shipment to preserve the in situ DO content in these samples, it is expected that the values reported here do not necessarily represent the *in situ* values. Figure 8-3 shows the geomean of all lysimeter DO measurements over time, highlighting the variability of this measurement in effluent samples. It is noteworthy that the majority of effluent samples are close to the theoretical saturation value of 8 mg L<sup>-1</sup> DO with an overall average value of  $7.55 \pm 1.88$  mg/L and  $7.61 \pm 1.74$  mg/L for the 200122 and 200311 sampling events, respectively. The 2014 winter samples were collected during the period of lowest temperature, thus it is surprising that these samples have the lowest average DO content. With the available data, an explanation for these low measurements is not possible. However, additional sampling events in 2015 and 2016 indicate that the samples have returned to approximately oxygen saturated conditions and that the low measurements during event 140210 appear to be an anomaly. Regardless, these anomalous fluctuations in DO content will be considered when examining radionuclide transport the lysimeters.



Figure 8-3: Average of all measured DO concentrations (mg L<sup>-1</sup>) for the lysimeter effluent samples for all sampling events to date. The average DO for all samples was 8.1 mg/L and the majority of samples were near this value except for the low measurements in lysimeters 14-2, 20-2, 21-3.

### 10. SUMMARY

In this work, the concentrations of radionuclides were measured in effluents from field lysimeters. These measurements are from the first six years of a long-term, multi-year experiment. Highlights from these measurements are:

- With the exception of three new PuO<sub>2</sub>NH<sub>4</sub>CO<sub>3</sub>(s) source lysimeters with 10% organic matter amended to the soil (lysimeters 14-2, 20-2, and 21-3), the concentrations of Pu in the effluents were below the ICP-MS detection limit for most lysimeters containing Pu sources. The amendment of organic matter resulted in the release of plutonium on the order of 10E-11 mol/L measured in two sampling events in January and March 2020. The effluents had lower dissolved oxygen, higher pH, and greater color than the other lysimeters. This implies that organic matter may have facilitated the transport of plutonium during this initial pulse of water through the lysimeter. However, this observation must be confirmed and examined further in future sampling events. Most other lysimeters maintained lower Pu concentrations in the effluent. An additional radioanalytical technique with a detection limit of approximately 10<sup>-15</sup> M demonstrated that there was measurable Pu in the effluent which was consistent with the release of Pu being a solubility-controlled phenomenon. This confirms previous studies demonstrating the relatively low mobility of Pu within SRS soils.
- Lysimeters 29 and 30, containing NpO<sub>2</sub>NO<sub>3</sub>(s) sources, have had measurable effluent concentrations of <sup>237</sup>Np corresponding to 1,558 Bq and 17,627 Bq. These values correspond to ~3% and ~38% of the initial source activity assuming a

45.88 kBq initial source<sup>2</sup>. This is consistent with the higher mobility of Np<sup>V</sup>. As in previous years, Np was also observed in the effluent of lysimeter 32, with a total of 51 Bq released, consistent with a relatively insoluble NpO<sub>2</sub>(s) source. The observation of Np in the effluent from this lysimeter implies oxidation of the NpO<sub>2</sub>(s) source, releasing Np<sup>V</sup>, which can transport through the lysimeter with a relatively low K<sub>d</sub>. It is noteworthy that lysimeters 29 (Np<sup>V</sup> source) and 31 (Np<sup>IV</sup> source) have been removed from the facility and the solid phase concentration of Np along the column has been measured. These results were published in Environmental Science and Technology as reported by Peruski et al., (2018).

<sup>60</sup>Co was the only gamma emitting radionuclide measured in the effluent samples until sampling event 180627, where breakthrough of <sup>137</sup>Cs and <sup>152</sup>Eu occurred in Lysimeters 27 and 28. The highest concentrations were observed in effluent from the lysimeters containing cement without added BFS, and the second highest effluent concentrations were from lysimeters containing saltstone sources. All cement and saltstone lysimeter sources contained higher concentrations of <sup>60</sup>Co in the effluent relative to a control with the gamma suite of radionuclides added directly to filter paper. However, this could be an artifact of the higher radionuclide concentration in the cement and saltstone lysimeters compared with

<sup>&</sup>lt;sup>2</sup> Evaluation of multiple NpO<sub>2</sub>(s) sources indicates some variability in the total <sup>237</sup>Np content in each source despite a similar level reported by Roberts et al., (2012). The variability is likely due to the difficulty of weighing small aliquots of solid actinide sources within a HEPA filtered glovebox at Savannah River National Laboratory. Thus, a better approach is to compare total activity leached and aqueous concentrations of each radioisotope in the effluent waters to evaluate the potential for solubility control of the aqueous concentration.

the filter paper source and overall similar fractions of the source have been released. The majority of the <sup>60</sup>Co was released within the first 2 years of the experiment and concentrations are now close to detection limits. It is unclear what is causing the enhanced mobility of <sup>60</sup>Co in the cement and saltstone sources.

• While the pH and DO values were variable for each lysimeter, the pH generally fell between 4.5 to 6.0 and the DO between 7 - 9 mg/L. Overall, the pH and DO has remained relatively constant for individual lysimeters. The geomean pH was 5.01 ± 0.66 for the most recent sampling interval and all values seem to converge around 5 (Appendix B, Table B.1). However, there is a large degree of variability in the volume of water passing through each lysimeter. Variations in the local conditions above the 4" diameter opening to the lysimeter could cause some of the observed differences. Tracer experiments demonstrated that the lysimeters have preferential flow paths which could also account for some of the differences in the volumes of water in the effluent.
## A. APPENDIX A – Supplemental materials and methods

Identification number for linking calibration data to sample measurements (Format: <i>Month-Year- Lab book Number-Lab book page</i> , where month and year are month and year of sample receipt from SRS).	11-12-1-2
Date of Sample Receipt from SRS	11/06/2012
Description of <sup>152</sup> Eu gamma spectroscopy standard (date of preparation, total activity, total volume, vessel)	11/14/12, 10.03 kBq/L, 45mL, 50mL conical centrifuge tube
Gamma spectrometer ID	HPGe (Model: GC4018, SN: 1933074)
Filename of gamma spectroscopy standard measurement	152Eu_std(HPGE6)_01112013
Filename of gamma spectroscopy background measurement	HPGE6_Background_111212
pH meter calibration slope and pH(0) value	98.1%, pH(0)=1.0233

## Datasheet for Instrument Calibration Documentation for 100412 Sampling Interval

Lysimeter number	2	
Sample ID	121004L2	
Date of sample collection at SRS	10/04/2012	
Date of sample receipt from SRS	11/06/2012	
Date of sample being prepared for analysis by Clemson	11/11/2012	
Date of analysis at Clemson	11/11/2012 (pH,DO), 11/16/2012 (HPGe)	
ID Number for Instrument Calibration data log sheet	11-12-1-2	

Table A-1:	Example	Data log	sheet for	Lysimeter	2 –	121004
I UDIC II II	L'Admpie	Data 10g	, sheet for	Lysincer	-	121001

Sample pH:	6.73
Sample Dissolved Oxygen Concentration (mg/L):	7.90
Mass of solution plus bottle (g)	653.11
Mass of solution subtracting average mass of collection bottles (g)	398.82

Estimated volume of solution removed for sample archiving (mL)	_
Archived sample ID:	-

Gamma detector ID used for analysis:	HPGe (Model: GC4018, SN: 1933074)
Gamma spectroscopy sample count filename:	45mL_SRS_100412L2_11162012.CNF

Table B.1: Geomean of pH values from all sampling events.			
Lysimeter number	Geomean	Lysimeter Number	Geomean
2	5.58	29	4.80
3	5.47	30	4.96
4	5.64	31	4.91
5	5.46	32	4.92
6	5.09	33	4.89
7	5.43	34	4.98
8	5.31	35	4.87
9	5.12	37	4.87
10	5.34	38	5.20
11	5.25	39	4.87
12	5.29	40	4.59
14	5.11	41	4.83
15	5.29	42	4.67
16	5.44	43	5.00
17	5.25	44	5.20
18	5.05	45	4.80
19	4.76	46	4.95
20	5.48	8-2	5.60
21	4.90	9-2	5.10
22	4.68	13-2	4.82
23	4.43	14-2	7.34
24	4.51	20-2	7.36
25	5.12	21-3	7.03
26	4.91	29-2	4.23
27	4.83	31-2	4.51
28	4.83		

APPENDIX B – Plots of pH versus time for all lysimeters

Β.























































C. APPENDIX C – Plots of dissolved oxygen (DO) versus time for all lysimeters




















































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