

OSR 45-11(Rev 10-22-2008)

Savannah River Site

Supplier Document Status

- 1.Work May Proceed
- 2.Submit Final Document - Work may proceed
- 3.Revise and Resubmit - Work may proceed subject to Resolution of Comments
- 4.Revise and Resubmit. Work may not Proceed.
- 5.Permission to proceed is not required.

Permission to proceed does not constitute acceptance or approval of design details, calculations, test methods, analysis or materials developed or selected by the supplier, and does not relieve supplier from full compliance with contractual obligations or release of any 'holds' placed on the contract.

Document ID

Revision

SRRA021685-000009

A

Document Category

Date

17.1-MTR (MATERIAL TEST REPORTS)

2017-12-13 08:22:52 AM, EST

Reviewer

KINARD, TIFFANY BROOKE

ENVIRONMENTAL ENGINEERING AND EARTH SCIENCES

L.G. Rich Environmental Laboratory

342 Computer Court

Anderson, SC 29625



Analysis of plutonium soil concentrations in field lysimeter experiments

Kathryn Peruski, Melody Maloubier, and Brian A. Powell

SRR Project Title: SRR Technical Support Provided by Clemson University

SRR PO number: SRRA021685SR

Report submitted in partial fulfillment of the scope of work outlined in SRR PO SRRA021685SR

Project PI: Brian A. Powell, bpowell@clemson.edu, 864.656.1004

Date Submitted: September 28, 2017

A handwritten signature in black ink, appearing to read 'B. Powell', written over a horizontal line.

Brian A. Powell
Principal Investigator, Technical Reviewer, QAQC reviewer

A handwritten date '9/28/17' in black ink, written over a horizontal line.

Date

A handwritten signature in black ink, appearing to read 'Jeremiah Mangold', written over a horizontal line.

Jeremiah Mangold, Savannah River Remediation, LLC

A handwritten date '11/15/2017' in black ink, written over a horizontal line.

Date

EXECUTIVE SUMMARY

This report describes the analysis of the spatial distribution of a 61 cm long x 10 cm diameter field lysimeter containing an end member soil and a $\text{PuO}_2(\text{s})$ source which was aged in the Savannah River Site, Radionuclide Field Lysimeter Experiments (RadFLEX) for 3.4 years. The lysimeter was retrieved from the RadFLEX facility and shipped to Clemson University where the lysimeter soil was segmented into 60 sections of approximately 1cm thickness. The concentration of Pu in each segment was determined using microwave-assisted acid digestion, ion exchange separation, and inductively coupled plasma mass spectroscopy. Consistent with previous lysimeter studies, both downward and upward migration of Pu was observed. A lower degree of upward migration is proposed to be due to the shorter time for Pu diffusion in the current lysimeter (3.4 years) compared with previous lysimeter studies (11 years). The downward transport of Pu in the current PuO_2 lysimeter was greater than that observed for previous PuCl_3 , $\text{Pu}(\text{NO}_3)_4$, and $\text{Pu}(\text{C}_2\text{O}_4)_2$ bearing lysimeters. This enhanced transport is hypothesized to be due to the colloidal nature of $\text{PuO}_2(\text{s})$ which could result in enhanced transport. However, this influence of colloids has not been experimentally confirmed. An alternative explanation is that the different initial chemical/physical state of the Pu source materials results in differing solubility values and thus, different migration behavior. Desorption experiments using Pu contaminated soils retrieved from this lysimeter indicated conditional desorption distribution coefficients of $\log K = 4.4 \pm 0.3$ L/kg. There was no apparent difference between unfiltered and ultrafiltered samples during the desorption experiments indicating that either 1) colloids are not present in these samples as hypothesized or 2) colloids sorb strongly to the soil and do not desorb. This working hypothesis must be experimentally confirmed through analysis of the source materials using microscopy and spectroscopy techniques.

1. Introduction

This document describes the analysis of the soil concentrations of Pu as a function of depth in lysimeter effluent from lysimeter #44 at the Radiological Field Lysimeter Experiment (RadFLEEx) at the Savannah River Site (SRS). This lysimeter contains a PuO₂(s) source consisting of 103 μCi ²³⁹Pu, 26 μCi ²⁴⁰Pu, and 917 μCi ²⁴¹Pu. The source consists of solid particles of PuO₂(s) sandwiched between two glass fiber filter papers. The filter paper is contained approximately half-way down in a field lysimeter which is 61 cm long x 10 cm diameter and filled with a vadose zone soil from the Savannah River Site. Additional details regarding the RadFLEEx facility are described in the report “SRNL Radionuclide Field Lysimeter Experiment: Baseline Construction and Implementation” by Roberts et al., [4]. The RadFLEEx results provide high pedigree data compared to previous laboratory data because it is conducted under controlled field conditions, under flow (not batch agitation) conditions, and for much longer durations. Additionally, results from the RadFLEEx will complement previously conducted lysimeter experiments [1-3, 5-7], by providing greater controls and ancillary information needed for less ambiguous assignment of transport mechanisms, including K_d values and oxidation and reduction reaction kinetics. Demonstrating understanding of and quantifying Pu transport in the vadose zone is especially important for predicting the risk posed by subsurface low level waste (LLW) disposal and emptied high level waste (HLW) tank disposition at the SRS.

2. Background

A series of field experiments were performed at the SRS during the 1980s in which a group of lysimeters containing sources of known Pu oxidation states were placed in the shallow subsurface. From 1981 until 1991 all lysimeters were left open to the environment except one, which was capped in 1983 and stored until it was analyzed. During this field period, aqueous leachate samples were collected and analyzed for gross alpha and beta activity; precipitation and climatic variables were recorded also. At the end of the open field period, all lysimeters were covered for an additional 5 yrs. Then these lysimeters were cored vertically, through the center, and the cores were stored in a cooler for an additional 6 yrs. After this time, various cores were sectioned, and Pu activities measured as a function of depth. Data from these lysimeters has been published and analyzed using a coupled reactive transport model in which rapid reduction of mobile Pu(V) to immobile Pu(IV) occurs upon interaction with soil minerals [1-3, 6, 8-10]. This behavior retards the downward migration of Pu. This mineral surface induced reduction of Pu(V) to Pu(IV) has been observed on a number of mineral phases [11-16]. However, there appears to be a slow oxidation step which slowly oxidizes a small fraction of the immobile Pu(IV) to mobile Pu(V) which results in enhanced downward transport. The conceptual model underlying this oxidation reaction is that rainwater with a high dissolved oxygen content transports through the lysimeter and generates a temporary oxidizing region in which Pu(V) can form and migrate through the soil before re-adsorbing to the mineral surface and reducing. The final reactive transport model included plant uptake to explain the upward migration of Pu [8-10]. The role of plants is especially important for composite analyses and for long term understanding of the fate of radionuclides once they escape the waste forms and enter into the environment. However, this phenomenon is outside our current scope of work as the lysimeter #44 analyzed in this report did not have plants growing in the lysimeter soil. It is noteworthy that there are several lysimeters with plants actively growing at this time [4]. Molz et al., [7] provide a detailed discussion of the reactive transport model and conceptual models underlying Pu transport in the previous set of field lysimeters.

While the reactive transport model presented by Demirkanli and co-workers has been capable of describing Pu transport in the lysimeters experiments from the 1980's, there are several assumptions in the model which require verification and a more complete analysis of the

chemical and physical evolution of the source term is required. The RadFLEx facility has lysimeters containing a variety of Pu sources including:

- $\text{Pu(V)NH}_4(\text{CO}_3)$ (lysimeters 21[#], 22[#], 23[#] and 41, 42, 43).
- $\text{Pu(III)}_2(\text{C}_2\text{O}_4)_3$ (lysimeters 33, 34, 35)
- $\text{Pu(IV)}(\text{C}_2\text{O}_4)_2$ (lysimeters 9*,10*,11* and 38, 39, 40)
- Pu(IV)O_2 colloids (lysimeters 44, 45, 46)

Lysimeters 9, 10, and 11 marked with “*” have grass plants actively growing on top. Lysimeters 21, 22, and 23 marked with “#” have been amended with 6% natural organic matter.

Additionally, there are four lysimeters containing Np(IV) and Np(V) sources for comparison with the similar redox speciation of the Pu lysimeters

- Np(IV)O_2 (lysimeters 31 and 32)
- $\text{Np(V)O}_2\text{NO}_3$ (lysimeters 29 and 30)

These source materials were utilized to examine the potential transformations of the source and the impacts on downward migration. The lysimeter experiments conducted in the 1980s included a Pu(VI) source. However, our geochemical analysis indicated that Pu(V) was likely the dominant oxidation state of Pu within the pore waters [17]. Therefore, a Pu(V) source ($\text{NH}_4\text{PuO}_2\text{CO}_3(\text{s})$) was included in these new experiments. Additionally, a $\text{PuO}_2(\text{s})$ was selected as all of the Pu sources are expected to transform to a $\text{PuO}_2(\text{s})$ type phase based on the strong thermodynamic stability of $\text{PuO}_2(\text{s})$. However, the kinetics of such transformations are unknown either in laboratory or field settings and the ultimate chemical and physical characteristics of the resulting $\text{PuO}_2(\text{s})$ are unknown. Many studies have observed disordered $\text{PuO}_2(\text{s})$ type phases forming but current research is yet to link the degree and nature of the disorder to the initial source conditions [18, 19]. Understanding these reaction pathways and the stability of these Pu sources under environmental conditions is critical to a robust performance assessment model because the oxidation state of the source, crystallinity, particle size, and potential co-precipitates can have an impact on the solubility of the source and eventual mobility of Pu from the source.

These new RadFLEx experiments have been started to validate our previous observations and quantify and characterize additional Pu sources with respect to vadose zone transport. These experiments are in the initial stages at this point and this report contains only the solid phase analysis of Pu from a $\text{PuO}_2(\text{s})$ source bearing lysimeter after approximately 3.4 years of exposure to field conditions (07/5/2012 to 11/5/2015). The concentration of Pu as a function of

distance away from the soil has been determined. Additionally, desorption experiments using the soil above and below the source have been performed to determine K_d values from a system under realistic environmental conditions.

3. Materials and Methods

Lysimeters removed from RadFLEX

The following five lysimeters were capped on October 8, 2015 and removed from RadFLEX for shipment to Clemson University on November 5, 2015.

- $\text{Pu(III)}_2(\text{C}_2\text{O}_4)_3$ (lysimeter 33)
- $\text{Pu(IV)}(\text{C}_2\text{O}_4)_2$ (lysimeters 38)
- $\text{Pu(IV)}\text{O}_2$ colloids (lysimeter 44)
- $\text{Np(IV)}\text{O}_2$ (lysimeters 31)
- $\text{Np(V)}\text{O}_2\text{NO}_3$ (lysimeters 29)

The lysimeters were stored in an upright position in a 55 gallon drum. For this work, lysimeter #44, $\text{PuO}_2(\text{s})$ source was analyzed. The lysimeter was removed from the drum on January 13, 2016 for and destructively sampled as described below.

Plutonium Lysimeter Soil Analysis

Lysimeters were kept in an upright position upon delivery to Clemson to preserve spatial distribution of Pu as best as possible. External containment and packaging was removed from the PVC pipe, which was transferred into a glove box and placed horizontally for coring. The glovebox contained atmospheric pressure and content but included a HEPA filtration system to avoid contamination of the lab with radionuclide bearing soils during sampling. Using a Dremel rotary tool with a cutting blade set to a depth to only cut the PVC pipe and not impact the soil, the lysimeter was cut along the longitudinal axis at two locations 180 degrees apart and again at the base near the filter to remove the 5cm to 10cm PVC reducer which hold the soil and filter in place at the bottom. The top half of the PVC was then removed to expose the intact soil core (Figure 1).

The length of the soil core was measured and pictures were taken to document the condition of the lysimeter upon arrival. The soil core was cut into approximately 1 cm segments using a stainless steel paint scraper which had been cut to have a round tip with a 5 cm radius that would fit into the 10 cm diameter PVC pipe and provide a clean section of soil. The length and location of each segment was recorded and each segment was stored in a pre-labelled



Figure 1. Photograph of intact soil lysimeter #44 in glove box, after removal of top half of PVC containment.

sampling bag. The lysimeter was cut from top down, taking care to cautiously identify and remove the source, then cut from the bottom back toward the source region, as described in Figure 2. After all soil had been separated into bags, all bags were removed from the glovebox and the weight of each bag was recorded. The source was placed in a separate bag and the “top” and “bottom” sections were noted on the bag using a permanent marker.

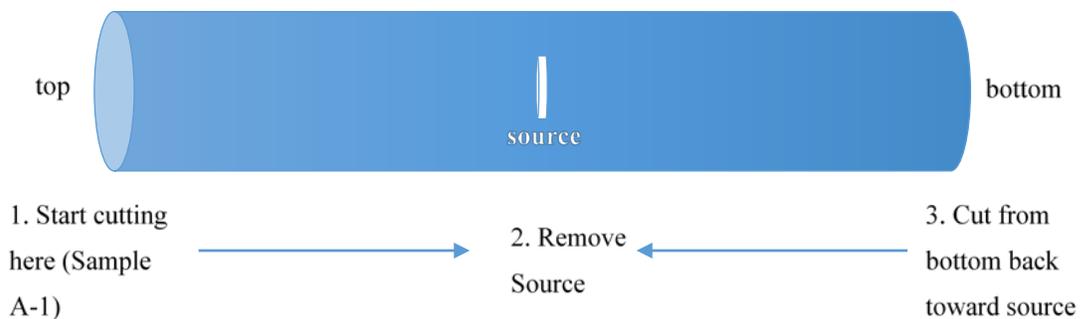


Figure 2: Diagram of sampling procedure

The source contained between two filter papers was placed in a separate bag for future analysis. The source, while in the bag, was exposed on an autoradiography plate for 15 minutes. For each 1 cm soil segment contained in a separate bag, sediment was homogenized by hand before sub-sampling. A 0.5 gram soil sample was taken from each segment and dried in an oven at 50 degrees Celsius for 2 days. Sample weights were recorded before and after drying to determine the water content in the soil sample. Dried soil samples were then placed in Teflon tubes for microwave digestion, and a known activity of ^{242}Pu tracer (0.05-0.07 Bq) was spiked into each sample. A 7mL aliquot of concentrated HNO_3 and 3mL of concentrated HF were added to each Teflon tube. Samples were run in a MARS microwave digestion system (CEM Corporation) using the EPA 3052 protocol [20].

After microwave digestion, remaining liquid in each tube was evaporated to dryness in Teflon beakers and then the residue was dissolved in 10mL of 9M HCl. Plutonium isotopes were extracted from this solution using anion exchange separation on pre-packed BioRad AG 1x8, chloride form columns with approximately 2 mL bed volumes. Columns were conditioned with 3 column volumes of 9M HCl before sample was added, then washed with 3 more column volumes of 9M HCl afterward. Plutonium was eluted from the ion exchange columns using three column volumes of 6M HCl/0.26M HF solution. The elution was evaporated to dryness in Teflon beakers, then dissolved in 2% nitric acid for analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). ICP-MS calibration standards for ^{239}Pu and ^{242}Pu were prepared using National Institute of Standards and Technology (NIST) standards 4330C and 4334I, respectively, and stock solutions traceable to these NIST standard. Samples were analyzed for ^{242}Pu and ^{239}Pu to determine the chemical yield and ^{239}Pu content in the lysimeter soil sample, respectively.

The concentration of ^{239}Pu in the soil sample was determined using equation 1:

$$[^{239}\text{Pu}]_{\text{soil}} = \frac{[^{239}\text{Pu}]_{\text{ICPMS}} \cdot V_{\text{ICPMS}}}{Y \cdot m_{\text{soil}}} \quad \text{Equation 1}$$

Where $[^{239}\text{Pu}]_{\text{ICPMS}}$ is the concentration of ^{239}Pu measured in the ICP-MS sample in mol/L, V_{ICPMS} is the volume of the ICP-MS samples in L, Y is the chemical yield of ^{242}Pu , and m_{soil} is the mass of soil initially added to the digestion tube in g. The purpose of the ^{242}Pu tracer was to determine the efficiency of Pu separation during the digestion and ion exchange process.

This recovery yield was used to correct for potential losses of ^{239}Pu during the separation. Thus, the final calculation is in $\text{mol}_{\text{Pu}}/\text{g}_{\text{soil}}$. Using the isotope ratios of ^{239}Pu and ^{240}Pu in the original source term, the total Pu concentration can be determined. For comparison with the activity levels reported in the original source, the mass units of ^{239}Pu were converted to activity using the ^{239}Pu half-life of 24,110 years.

Desorption Experiments

Desorption experiments were conducted on soils from approximately 3 cm above and below the PuO_2 source. Four locations were chosen in order to evaluate if there is any change according to the depth. The samples contained between 170 and 3560 Bq $^{239}\text{Pu}/\text{g}_{\text{sediment}}$. A 1 g aliquot of sediment was placed in a 15 mL centrifuge tube containing 10 mL of 10 mM NaCl with triplicate samples prepared for each section. The suspensions were placed on a slow moving platform shaker for 14 days. After 14 days of mixing, the samples were centrifuged at 8000 rpm for 20 minutes in a Beckman C1015 rotor which is calculated to remove particles greater than 100 nm from solution based on Stokes law [21]. The solid and aqueous phases were separated and an aliquot of the supernatant was passed through a 30K MWCO ultrafilter (Microsep Advance Centrifugal device; Pall Corporation). Total Pu concentration in the supernatant and filtrate were measured by LSC (Quantulus, Perkin-Elmer) before and after filtration, by mixing 1 mL of the supernatant or filtrate with 19 mL of HiSafe III LSC cocktail (Perkin Elmer). Each sample was counted on the Quantulus for one hour. For each sample, the K_d was calculated by taking the ratio of the Pu concentration in the soil and in the aqueous phase after 14 days of desorption. As equilibrium cannot be guaranteed after only 14 days, these K_d values should be considered conditional values.

Analysis of Pu activity in filter paper source

To measure the activity of ^{239}Pu remaining in the source after exposure in the environment, source filter paper was placed in a 4" diameter petri dish and measured on a low-energy high purity germanium detector (HPGe). Only ^{239}Pu was measured because ^{240}Pu and ^{241}Pu do not have gamma energies with emission fractions high enough for measurement. The source was counted for 2000 seconds on a Marinelli beaker to reduce dead time and background

corrected. Two energies were used to determine the activity of ^{239}Pu (Table 1) in order to verify the measurement.

Table 1. Peak Energy, emission fraction, and efficiency for ^{239}Pu

Isotope	Peak Energy (keV)	Emission Fraction	Peak Efficiency
^{239}Pu	51.8	0.00027	0.0087
^{239}Pu	129.6	0.00006	0.0074

The efficiency of each peak was determined using a filter paper standard, prepared by spiking a known activity of NIST-calibrated ^{239}Pu onto a filter paper, placed in a 4" petri dish and measured using the same geometry as the source. The efficiency was determined according to equation 2:

$$\text{Efficiency } (E) = \frac{(n_G - n_B)}{A * t * F} \quad \text{Equation 2}$$

where n_G and n_B are gross and background counts in the region of interest, respectively, A is the activity of ^{239}Pu in the standard spike, t is the count time, and F is the emission fraction. The activity of ^{239}Pu was determined using equation 3:

$$A = \frac{(n_G - n_B)}{t * F * E} \quad \text{Equation 3}$$

4. Results & Discussion

The soil and source material were all successfully removed and separated during coring. The source (Figure 3, left) filter paper still contained visible $\text{PuO}_2(\text{s})$ as indicated by the green color. Autoradiography image of the source (Figure 3, right) confirms the presence of radioactivity in the greenish region visible in the picture of the source. Autoradiography images cannot give quantitative measure of remaining activity in the source.



Figure 3: Picture (left) and autoradiography image (right) of lysimeter 44 source. Images are to scale.

Complete soil sampling data, including segment lengths, locations, and total mass of soil per segment, can be found in Appendix Table 1. Volumetric water content for each soil subsection for Lysimeter 44 ranged from 10-20% (Figure 4), with higher water content near the base of the lysimeter, consistent with gravity induced drainage of the lysimeter. Complete data for water content can be found in Appendix Table 2.

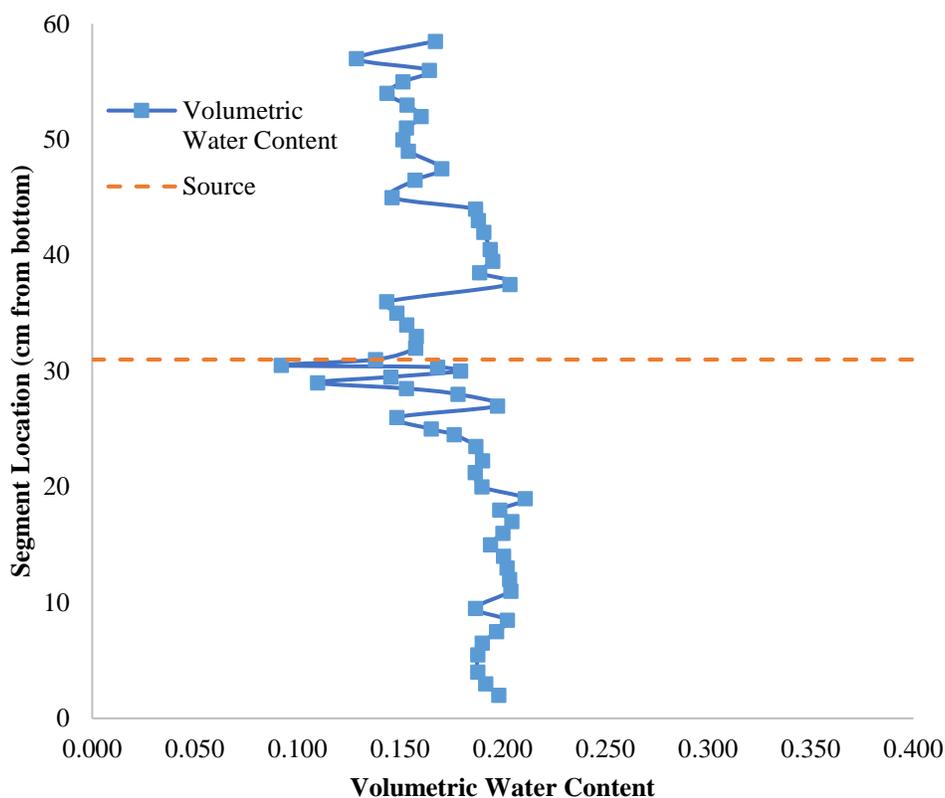


Figure 4: Volumetric water content as a function of location in the lysimeter, where 0 is the base of the lysimeter and 58.5 cm is the top. Source is located at 31 cm.

Soil digestions and ion exchange had an average chemical yield for ^{242}Pu of 9.5%. The low yield may be attributed to a number of factors, including interference with high iron concentrations from the soil digestate and high flow rates through pre-packed ion exchange columns. Reported concentrations of ^{239}Pu (in Bq/g) account for the chemical yield in each sample as noted in equation 1. A complete table of Pu concentrations is given in Appendix Table 3. The minimum detectable concentration (MDC) provides a lower limit on the concentration of ^{239}Pu which can be reliably measured and is based on the sensitivity and detection limit of the ICP-MS corrected for dilution as noted in equation 4. An example calibration curve for ICPMS determination of ^{239}Pu is shown in the Appendix (Figure A1). The ICP-MS detection limit was 2.0×10^{-6} ppb based on the calibration curve in Figure A1. This value was corrected for the chemical yield (Y), ICPMS sample volume (V_{ICPMS}), and mass of digested soil (m_{soil}) shown in equation 4 where $[\text{}^{239}\text{Pu}]_{\text{DL,ICPMS}}$ is the ICPMS detection limit.

$${}^{239}\text{Pu} - \text{MDC} = \frac{[{}^{239}\text{Pu}]_{DL,ICPMS} * V_{ICPMS}}{\gamma * m_{soil}} \quad \text{Equation 4.}$$

The MDC was 5.79×10^{-4} Bq/g and all positive measurements of ${}^{239}\text{Pu}$ were at least one order of magnitude above the detection limit.

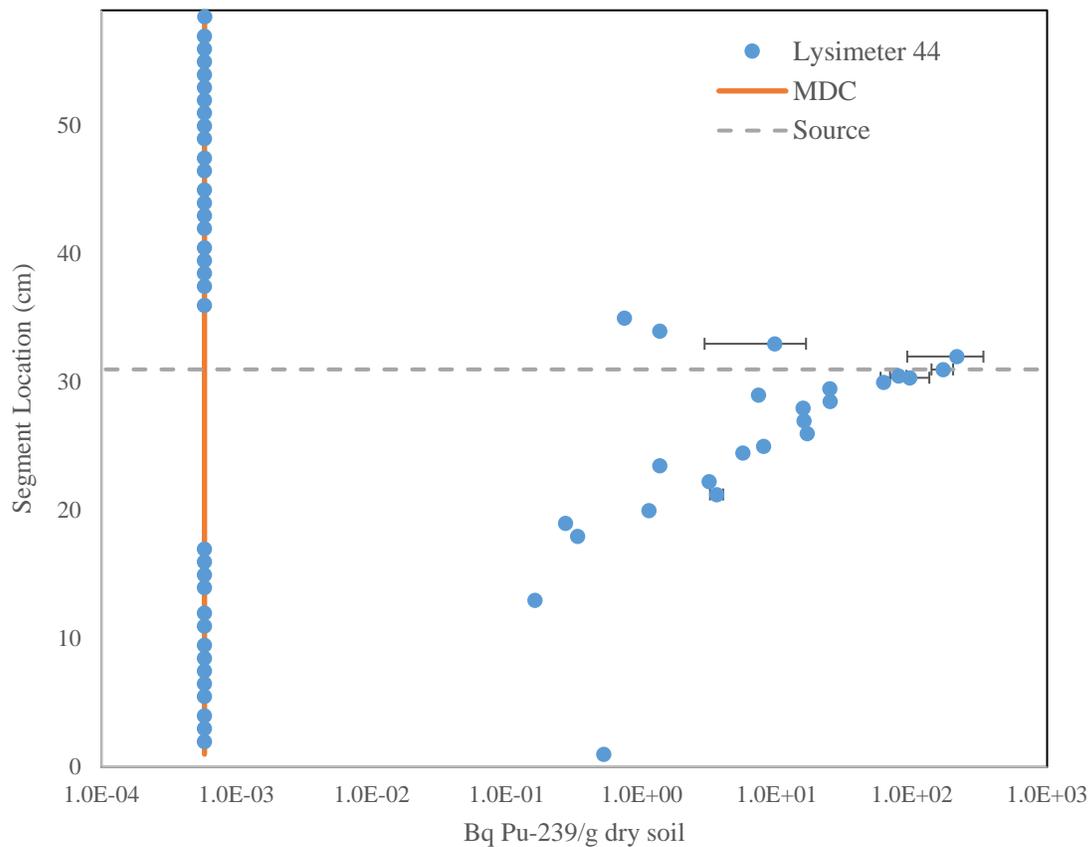


Figure 5. ${}^{239}\text{Pu}$ concentration (in Bq/g) for Lysimeter 44 soil samples as a function of location in the lysimeter, where 0 cm is the base and 58.5 cm is the top. Standard deviation calculated from standard deviation of ICP-MS measurements. MDC= minimum detectable concentration, calculated from ICP-MS measurements.

${}^{239}\text{Pu}$ transport was observed 13 cm below source, with maximum concentrations at approximately 350 Bq/g (Figure 5). Two data points exist at 18 cm and 30 cm below source showing measurable ${}^{239}\text{Pu}$, where all points surrounding have no measurable ${}^{239}\text{Pu}$ above the MDC. These data points may represent “hot spots”, where Pu has preferentially concentrated as compared to surrounding material or possibly an artifact of sampling (with a small amount of Pu

bearing soil contaminating the lower soil subsamples) or analytical analysis. Also, the sample at 30 cm below source is the base of the lysimeter, where Pu may have concentrated at the junction of the soil and the nylon screen filter, increasing the concentration in the soil. This hypothesis is supported by the effluent reports produced by Clemson University, showing using low-level measurements that ^{239}Pu can be measured in effluent samples from Pu lysimeters at RadFLEX [22], indicating that Pu has moved to the base of the lysimeter. Above source, ^{239}Pu is measured up to 4 cm above source, but quickly dropped below detection limits (Figure 5).

A comparison of previously analyzed Pu lysimeters from SRS shows similar scale of Pu transport from a range of Pu source materials (Figure 6). The PuO_2 lysimeter analyzed in this work (green markers in Figure 6) shows slightly enhanced transport (an increase of a few cm) below the source as compared to the other Pu lysimeters. Upward transport from the PuO_2 lysimeter is slightly decreased ($<1\text{cm}$) as compared to the other Pu lysimeters. Assuming that the upward migration near the source was due to diffusion, the slight decrease in the PuO_2 relative to the other lysimeters was likely due to the shorter time in the field of the PuO_2 lysimeter (3.4 years) relative to the other lysimeters (11 years) [1-3]. Without further modeling analysis, it is difficult to determine if the observation of greater downward migration of Pu in the PuO_2 lysimeter is significant. It is assumed that a similar oxidation-reduction process will control the migration of Pu within the PuO_2 system as it did for the other lysimeters. As discussed above, formation of PuO_2 from the PuCl_3 , $\text{Pu}(\text{NO}_3)_4$, and $\text{Pu}(\text{C}_2\text{O}_4)_2$ lysimeters is expected but the rates are unknown at this point and it is hoped that these new RadFLEX experiments will provide such information.

The other major difference between the PuO_2 lysimeter and other Pu lysimeters is the potential for colloidal transport of Pu. The PuO_2 source was prepared by rapid neutralization of an acidic Pu(IV) stock solution. Powell et al., [23] has shown this is a means of producing crystalline, nanometer scale PuO_2 particles from bulk precipitation. Actinide elements can form colloidal species, either through hydrolysis of actinide cations to form “intrinsic” colloids or through adsorption of actinide cations to inorganic or organic constituents in groundwater to form “pseudo” or “associative” colloids [24-26]. Actinides in the (IV) oxidation state show the greatest affinity for formation of intrinsic colloids, and the (IV) oxidation state is also likely to form pseudo colloids due to its high sorption affinity to organic or inorganic matter [27-29]. Thus, one working hypothesis to explain the downward migration of Pu from the PuO_2

lysimeter could be that colloidal particles have been freed from the aggregated bulk precipitate and migrated further down the column. This is also a potential explanation for the presence of elevated concentrations of ^{239}Pu near the base of the lysimeter (Figure 6).

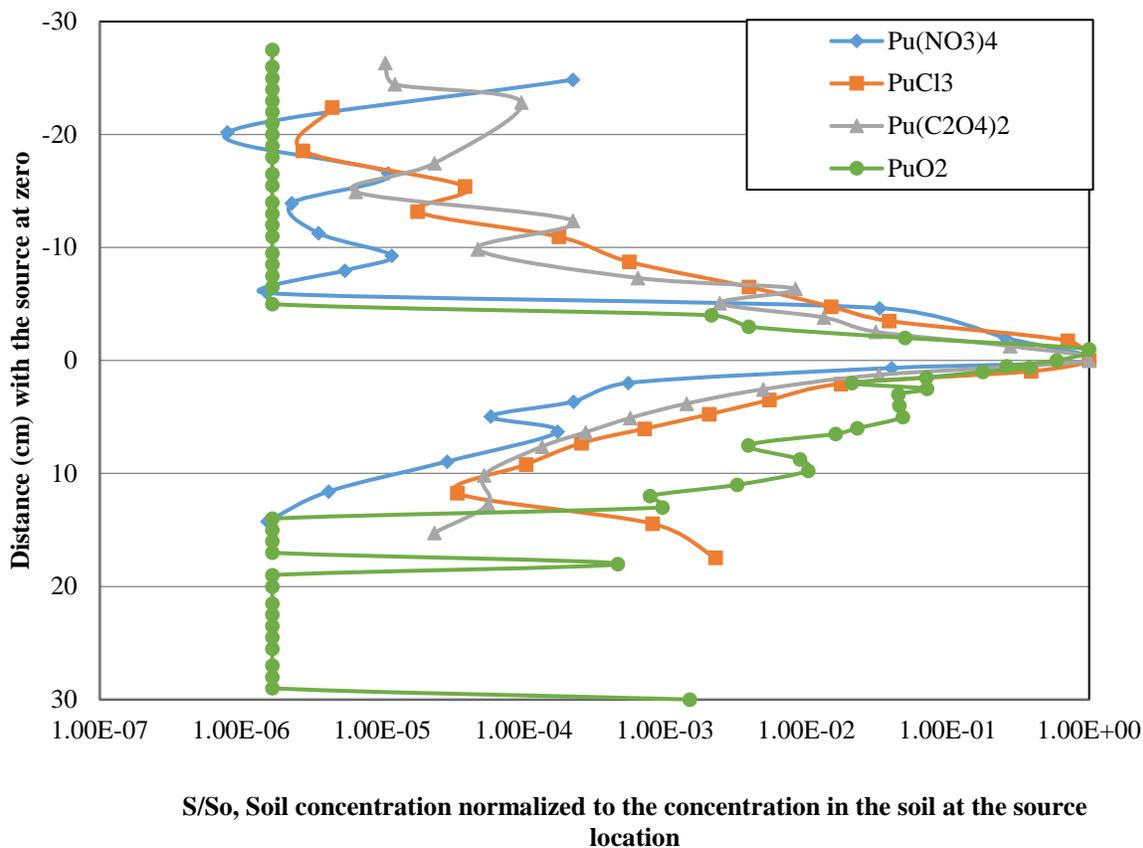


Figure 6. Comparison of Pu transport from lysimeters of varying Pu source material. Concentrations are normalized to the maximum concentration at the source region. Data for $\text{Pu}(\text{NO}_3)_4$, PuCl_3 , and $\text{Pu}(\text{C}_2\text{O}_4)_2$ lysimeters from [1-3].

Batch desorption experiments

Presence of such Pu(IV) colloids could greatly affect transport of Pu through natural systems, given the potential for highly different environmental behavior than simple aqueous ionic species of Pu. Further studies of soil samples from Pu lysimeters are necessary to identify the presence of colloidal species, such as desorption experiments and XAS studies of specific soil samples. A limited set of desorption experiments was conducted on soil samples from near the source region (Table 2). These are referred to as conditional desorption K_d values because the samples were analyzed only after 14 days of desorption and equilibrium cannot be assumed.

After desorption, the average sorbed fraction remaining on the sediment is 99.9% of the initial Pu and log K_d values for filtered samples vary between 4.32 and 4.85 and for unfiltered samples vary from 4.04 to 4.62. The values obtained are in good agreement with the K_d values obtained previously from desorption experiments of sediment amended with $\text{NH}_4\text{Pu}^{\text{V}}\text{O}_2\text{CO}_3$ and sediment amended with a $\text{Pu}^{\text{IV}}(\text{NO}_3)$ source from previous lysimeter field studies. The estimated log K_d values were equal to 3.2-4.2 [30].

However, there was no apparent difference between the desorption K_d values from samples above or below the immediate source region. Though only supported by indirect evidence, this would indicate that the chemical species of Pu associated with the soil is the same directly above and below the source region. Knowing that upward migration of colloids is unlikely, this would indicate that the sorbed Pu within this region is present as monomeric, sorbed Pu. However, further analysis is needed to confirm this working hypothesis and analysis of samples from greater depths, such as those located at 18 and 30 cm below the source, is needed.

Table 2: Aqueous and soil concentrations of Pu along with calculated desorption conditional K_d values (noted as *) from the desorption experiments with soils from near the source region of lysimeter 44. Data obtained after 14 days of equilibrium (F: filtered, UF: unfiltered). Experiments run at pH 5 which is the natural buffering pH of the soil. Note: unfiltered samples were centrifuged 20 minute at 8000 rpm in a Beckman C1015 rotor which is calculated to remove particles greater than 100 nm from solution based on Stokes law [21]

Sample Name	Pu aqueous concentration (Bq/ml)	Pu soil concentration (Bq/g)	K_d^* (ml/g)	Average K_d^* (ml/g)	standard deviation (ml/g)	Log K_d^*
F-44-A-27-1	0.1327	2090.9	15761	20738	4829	4.32
F-44-A-27-2	0.0823	2090.9	25405			
F-44-A-27-3	0.0993	2090.9	21049			
F-44-A-25-1	0.1658	3557.8	21462	27994	13027	4.45
F-44-A-25-2	0.0828	3557.9	42994			
F-44-A-25-3	0.1822	3557.8	19525			
F-44-B-31-1	0.0149	629	42192	48266	10483	4.68
F-44-B-31-2	0.0104	629	60371			
F-44-B-31-3	0.0149	629	42234			
F-44-B-26-1	0.0065	171	26412	69963	53104	4.85
F-44-B-26-2	0.0031	171	54355			
F-44-B-26-3	0.0013	171	129121			

Sample Name	Pu aqueous concentration (Bq/ml)	Pu soil concentration (Bq/g)	Kd* (ml/g)	Average Kd* (ml/g)	standard deviation (ml/g)	Log Kd*
UF-44-A-27-1	0.1324	2090.9	15798	16961	3684	4.23
UF-44-A-27-2	0.0992	2090.9	21087			
UF-44-A-27-3	0.1494	2090.9	13999			
UF-44-A-25-1	0.2147	3557.8	16573	14452	3638	4.16
UF-44-A-25-2	0.2152	3557.8	16531			
UF-44-A-25-3	0.3471	3557.7	10251			
UF-44-B-31-1	0.022	629	28557	41166	23234	4.62
UF-44-B-31-2	0.0093	629	67978			
UF-44-B-31-3	0.0233	629	26963			
UF-44-B-26-1	0.0288	171	5939	10853	5255	4.046
UF-44-B-26-2	0.0167	171	10229			
UF-44-B-26-3	0.0104	171	16392			

Analysis of Pu activity in the recovered source and activity balance calculations

To complete the activity balance in Lysimeter 44, it is important to note that no ^{239}Pu was measured in the effluent over the course of 3 years. The total activity of ^{239}Pu in the soil was determined by extrapolating the concentration in each section of the soil for the entire soil segment, according to Equation 5:

$$A_T = A_S * m \quad \text{Equation 5}$$

where A_T is the total activity (in Bq), A_S is the activity in the segment (Bq/g), and m is the total mass of soil in the segment. The total activity in Lysimeter 44 sediment is 72.76 kBq (SD 1.386 kBq), corresponding to 1.9% (SD 0.036%) of the total ^{239}Pu from the initial source. In total, summation of the lysimeter soil activity from each segment plus the measured source activity can account for greater than 90% of the total ^{239}Pu that was initially employed in the lysimeter.

5. Summary

Analysis of lysimeter 44 containing a PuO_2 source indicated both downward as well as a slight upward migration of Pu. The upward migration of Pu was decreased relative to several previous lysimeters. This difference is proposed to be due to the shorter deployment time of the current lysimeter (3.4 years) compared with the previous lysimeter studies (11 years) which allowed for less time for upward diffusion. The downward transport of Pu in the current PuO_2 lysimeter was greater than that observed for previous PuCl_3 , $\text{Pu}(\text{NO}_3)_4$, and $\text{Pu}(\text{C}_2\text{O}_4)_2$ bearing lysimeters. This enhanced transport is hypothesized to be due to the colloidal nature of $\text{PuO}_2(\text{s})$ which could result in enhanced transport. The PuO_2 source was prepared using a method known to produce 3-5 nm PuO_2 colloids [23]. However, this influence of colloids has not been experimentally confirmed. An alternative explanation is that the different initial chemical/physical state of the Pu source materials results in differing solubility values and thus, different migration behavior. Desorption experiments using Pu contaminated soils retrieved from this lysimeter indicated conditional desorption distribution coefficients of $\log K = 4.4 \pm 0.3$ L/kg. There was no apparent difference between unfiltered and ultrafiltered samples during the desorption experiments indicating that either 1) colloids are not present in these samples as hypothesized or 2) colloids sorb strongly to the soil and do not desorb. The latter is supported by observations of strong binding of PuO_2 colloids to iron oxide surfaces [23]. This working hypothesis must be experimentally confirmed through analysis of the source materials using microscopy and spectroscopy techniques.

6. Appendix

Table A1. Soil Sampling Data from Lysimeter 44

Sample ID	Segment Length (cm)	Location	Mass of soil + bag (g)
44-A-1	1.5	58.5 cm from bottom; Position 57-58.5 cm; TOP	166.5
44-A-2	1	57 cm from bottom; Position 56-57 cm	94.5
44-A-3	1	56 cm from bottom; Position 55-56 cm	115.5
44-A-4	1	55 cm from bottom; Position 54-55 cm	178.5
44-A-5	1	54 cm from bottom; Position 53-54 cm	105.0
44-A-6	1	53 cm from bottom; Position 52-53 cm	145.5
44-A-7	1	52 cm from bottom; Position 51-52 cm	166.0
44-A-8	1	51 cm from bottom; Position 50-51 cm	174.0
44-A-9	1	50 cm from bottom; Position 49-50 cm	179.0
44-A-10	1.5	49 cm from bottom; Position 47.5-49 cm	202.5
44-A-11	1	47.5 cm from bottom; Position 46.5-47.5 cm	214.5
44-A-12	1.5	46.5 cm from bottom; Position 45-46.5 cm	186.0
44-A-13	1	45 cm from bottom; Position 44-45 cm	146.5
44-A-14	1	44 cm from bottom; Position 43-44 cm	171.5
44-A-15	1	43 cm from bottom; Position 42-43cm	144.5
44-A-16	1.5	42 cm from bottom; Position 40.5-42 cm	146.5
44-A-17	1	40.5 cm from bottom; Position 39.5-40.5 cm	154.0
44-A-18	1	39.5 cm from bottom; Position 38.5-39.5 cm	130.0
44-A-19	1	38.5 cm from bottom; Position 37.5-38.5 cm	170.5
44-A-20	1.5	37.5 cm from bottom; Position 36-37.5 cm	208.0
44-A-21	1	36 cm from bottom; Position 35-36 cm	138.5
44-A-22	1	35 cm from bottom; Position 34-35 cm	136.0
44-A-23	1	34 cm from bottom; Position 33-34 cm	169.0
44-A-24	1	33 cm from bottom; Position 32-33 cm	128.5
44-A-25	1	32 cm from bottom; Position 31-32 cm, in contact with source	94.0
44-A-26	no length	source located at 31 cm, had minimal soil attached; SOURCE	N/A
44-A-27	0.5	31 cm from bottom; Position 30.5-31 cm, in contact with source	46.5
44-A-28	0.15	30.5 cm from bottom; Position 30.35-30.5 cm	43.5
44-B-32	0.35	30.35 cm from bottom; Position 30-30.35 cm	111.5
44-B-31	0.5	30 cm from bottom; Position 29.5-30 cm	84.5
44-B-30	0.5	29.5 cm from bottom; Position 29-29.5 cm	75.5
44-B-29	0.5	29 cm from bottom; Position 28.5-29 cm	63.5
44-B-28	0.5	28.5 cm from bottom; Position 28-28.5 cm	66.5
44-B-27	1	28 cm from bottom; Position 27-28 cm; lysimeter crumbling	82.0

Sample ID	Segment Length (cm)	Location	Mass of soil + bag (g)
44-B-26	1	27 cm from bottom; Position 26-27 cm	96.0
44-B-25	1	26 cm from bottom; Position 25-26 cm	116.0
44-B-24	0.5	25 cm from bottom; Position 24.5-25 cm	100.5
44-B-23	1	24.5 cm from bottom; Position 23.5-24.5 cm	128.5
44-B-22	1.25	23.5 cm from bottom; Position 22.25-23.5 cm	175.0
44-B-21	1	22.25 cm from bottom; Position 21.25-22.25 cm	123.0
44-B-20	1.25	21.25 cm from bottom; Position 20-21.25 cm	157.5
44-B-19	1	20 cm from bottom; Position 19-20 cm	141.0
44-B-18	1	19 cm from bottom; Position 18-19 cm	156.0
44-B-17	1	18 cm from bottom; Position 17-18 cm	189.5
44-B-16	1	17 cm from bottom; Position 16-17 cm	164.0
44-B-15	1	16 cm from bottom; Position 15-16 cm	182.0
44-B-14	1	15 cm from bottom; Position 14-15 cm	166.0
44-B-13	1	14 cm from bottom; Position 13-14 cm	159.5
44-B-12	1	13 cm from bottom; Position 12-13 cm	160.0
44-B-11	1	12 cm from bottom; Position 11-12 cm	163.5
44-B-10	1.5	11 cm from bottom; Position 9.5-11 cm	151.5
44-B-9	1	9.5 cm from bottom; Position 8.5-9.5 cm	155.0
44-B-8	1	8.5 cm from bottom; Position 7.5-8.5 cm	155.0
44-B-7	1	7.5 cm from bottom; Position 6.5-7.5 cm	163.0
44-B-6	1	6.5 cm from bottom; Position 5.5-6.5 cm	151.5
44-B-5	1.5	5.5 cm from bottom; Position 4-5.5 cm	140.0
44-B-4	1	4 cm from bottom; Position 3-4 cm	175.0
44-B-3	1	3 cm from bottom; Position 2-3 cm	144.5
44-B-2	1	2 cm from bottom; Position 1-2 cm	166.0
44-B-1	1	Top edge is 1 cm from bottom; Position 0-1 cm; BOTTOM	220.0

Table A2. Volumetric water content data for lysimeter 44

Sample ID	Segment Location (cm from bottom)	Volumetric Water Content (cm ³ water per cm ³ soil)
44-A-1	58.5	0.167
44-A-2	57	0.129
44-A-3	56	0.164
44-A-4	55	0.151
44-A-5	54	0.144
44-A-6	53	0.153
44-A-7	52	0.160
44-A-8	51	0.153
44-A-9	50	0.151
44-A-10	49	0.154
44-A-11	47.5	0.170
44-A-12	46.5	0.157
44-A-13	45	0.146
44-A-14	44	0.187
44-A-15	43	0.188
44-A-16	42	0.191
44-A-17	40.5	0.194
44-A-18	39.5	0.195
44-A-19	38.5	0.189
44-A-20	37.5	0.203
44-A-21	36	0.143
44-A-22	35	0.148
44-A-23	34	0.153
44-A-24	33	0.158
44-A-25	32	0.158
44-A-27	31	0.138
44-A-28	30.5	0.092
44-B-32	30.35	0.168
44-B-31	30	0.179
44-B-30	29.5	0.145
44-B-29	29	0.110
44-B-28	28.5	0.153
44-B-27	28	0.178
44-B-26	27	0.197
44-B-25	26	0.148
44-B-24	25	0.165

Sample ID	Segment Location (cm from bottom)	Volumetric Water Content (cm ³ water per cm ³ soil)
44-B-23	24.5	0.176
44-B-22	23.5	0.187
44-B-21	22.25	0.190
44-B-20	21.25	0.186
44-B-19	20	0.190
44-B-18	19	0.211
44-B-17	18	0.199
44-B-16	17	0.204
44-B-15	16	0.200
44-B-14	15	0.194
44-B-13	14	0.200
44-B-12	13	0.202
44-B-11	12	0.203
44-B-10	11	0.204
44-B-9	9.5	0.187
44-B-8	8.5	0.202
44-B-7	7.5	0.197
44-B-6	6.5	0.190
44-B-5	5.5	0.188
44-B-4	4	0.188
44-B-3	3	0.192
44-B-2	2	0.198
44-B-1	1	0.204

Table A3. ²³⁹Pu concentration (in Bq/g) for lysimeter 44 soil samples. Standard deviation calculated from standard deviation of ICP-MS measurements. MDC= minimum detectable concentration, calculated from ICP-MS measurements equal to 5.79 x 10⁻⁴ Bq/g..

Sample ID	Bq Pu-239/g dry soil	Standard Deviation (Bq/g)	Segment Location (cm from bottom)
44-A-1	0	0	58.5
44-A-2	0	0	57
44-A-3	0	0	56
44-A-4	0	0	55
44-A-5	0	0	54
44-A-6	0	0	53
44-A-7	0	0	52
44-A-8	0	0	51
44-A-9	0	0	50
44-A-10	0	0	49
44-A-11	0	0	47.5
44-A-12	0	0	46.5
44-A-13	0	0	45
44-A-14	0	0	44
44-A-15	0	0	43
44-A-16	0	0	42
44-A-17	0	0	40.5
44-A-18	0	0	39.5
44-A-19	0	0	38.5
44-A-20	0	0	37.5
44-A-21	0	0	36
44-A-22	0.74	0	35
44-A-23	1.36	0	34
44-A-24	17.44	1.77	33
44-A-25	349.43	7.25	32
44-A-27	205.33	2.45	31
44-A-28	90.99	0.65	30.5
44-B-32	132.50	1.85	30.35
44-B-31	61.79	1.04	30
44-B-30	24.69	0.20	29.5
44-B-29	7.30	0	29
44-B-28	24.84	0.21	28.5
44-B-27	15.60	0.54	28

Sample ID	Bq Pu-239/g dry soil	Standard Deviation (Bq/g)	Segment Location (cm from bottom)
44-B-26	15.89	0	27
44-B-25	16.78	0.52	26
44-B-24	7.98	0	25
44-B-23	5.61	0	24.5
44-B-22	1.36	0	23.5
44-B-21	3.15	0	22.25
44-B-20	3.60	0.40	21.25
44-B-19	1.13	0	20
44-B-18	0.27	0	19
44-B-17	0.33	0	18
44-B-16	0	0	17
44-B-15	0	0	16
44-B-14	0	0	15
44-B-13	0	0	14
44-B-12	0.16	0	13
44-B-11	0	0	12
44-B-10	0	0	11
44-B-9	0	0	9.5
44-B-8	0	0	8.5
44-B-7	0	0	7.5
44-B-6	0	0	6.5
44-B-5	0	0	5.5
44-B-4	0	0	4
44-B-3	0	0	3
44-B-2	0	0	2
44-B-1	0.52	0	1

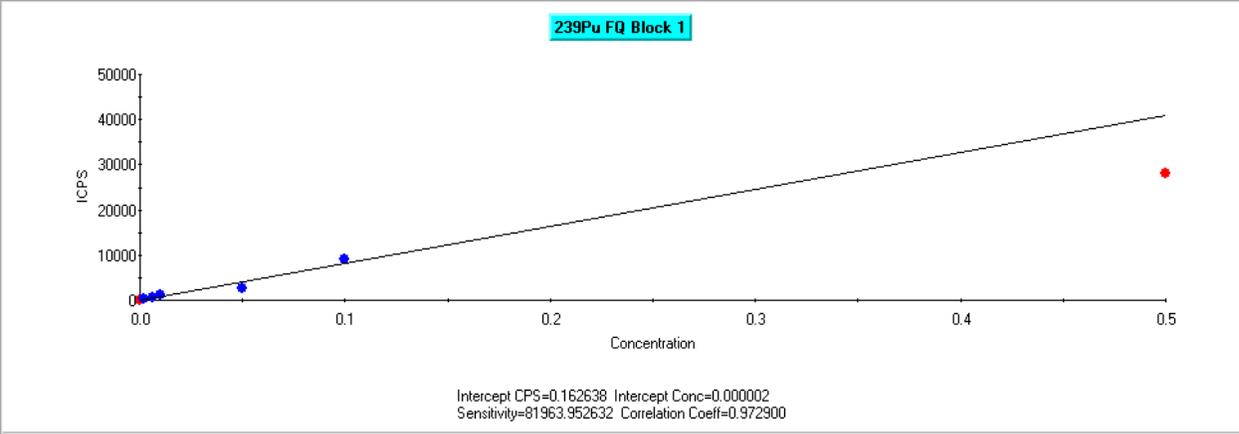


Figure A1: ICPMS calibration curve for 239Pu. Thermo X Series II ICPMS

7. References

1. Kaplan, D.I., et al., *Eleven-year field study of Pu migration from PuIII, IV, and VI sources*. Environmental Science & Technology, 2006. **40**(2): p. 443-448.
2. Kaplan, D.I., et al., *Influence of oxidation states on plutonium mobility during long-term transport through an unsaturated subsurface environment*. Environmental Science & Technology, 2004. **38**(19): p. 5053-5058.
3. Kaplan, D.I., et al., *Influence of sources on plutonium mobility and oxidation state transformations in vadose zone sediments*. Environmental Science & Technology, 2007. **41**(21): p. 7417-7423.
4. Roberts, K.A., et al., *SRNL Radionuclide Field Lysimeter Experiment: Baseline Construction and Implementation*. 2012, Savannah River National Laboratory Aiken, SC
5. Kaplan, D.I., et al., *Long-Term Radiostrontium Interactions and Transport through Sediment*. Environmental Science & Technology, 2014. **48**(15): p. 8919-8925.
6. Kaplan, D.I., et al., *Influence of pH on plutonium desorption/solubilization from sediment*. Environmental Science & Technology, 2006. **40**(19): p. 5937-5942.
7. Molz, F., et al., *Plutonium transport in soil and plants: An interdisciplinary study motivated by lysimeter experiments at the Savannah River Site*, in *Dynamics of fluids and transport in complex fractured-porous systems*, B. Faybishenko, S.M. Benson, and J.E. Gale, Editors. 2015, Co-publication: American Geophysical Union and John Wiley and Sons, Inc. : Washington DC and Hoboken, NJ. p. 183-208.
8. Demirkanli, D.I., et al., *A fully transient model for long-term plutonium transport in the Savannah River Site vadose zone: Root water uptake*. Vadose Zone Journal, 2008. **7**(3): p. 1099-1109.
9. Demirkanli, D.I., et al., *Soil-Root Interactions Controlling Upward Plutonium Transport in Variably Saturated Soils*. Vadose Zone Journal, 2009. **8**(3): p. 574-585.
10. Demirkanli, D.I., et al., *Modeling long-term plutonium transport in the Savannah River Site vadose zone*. Vadose Zone Journal, 2007. **6**(2): p. 344-353.
11. Sanchez, A.L., J.W. Murray, and T.H. Sibley, *The Adsorption of Plutonium-Iv and Plutonium-V on Goethite*. Geochimica Et Cosmochimica Acta, 1985. **49**(11): p. 2297-2307.
12. Keeney-Kennicutt, W.L. and J.W. Morse, *The redox chemistry of Pu(V)O₂⁺ interaction with common mineral surfaces in dilute solutions and seawater*. Geochimica et Cosmochimica Acta, 1985. **49**(12): p. 2577-2588.
13. Hixon, A.E., et al., *Influence of iron redox transformations on plutonium sorption to sediments*. Radiochimica Acta, 2010. **98**(9-11): p. 685-692.
14. Powell, B.A., et al., *Plutonium oxidation and subsequent reduction by Mn(IV) minerals in Yucca Mountain tuff*. Environ Sci Technol, 2006. **40**(11): p. 3508-14.
15. Powell, B.A., et al., *Pu(V)O₂⁺ adsorption and reduction by synthetic magnetite (Fe₃O₄)*. Environmental Science & Technology, 2004. **38**(22): p. 6016-6024.
16. Powell, B.A., et al., *Pu(V)O₂⁺ adsorption and reduction by synthetic hematite and goethite*. Environmental Science & Technology, 2005. **39**(7): p. 2107-2114.
17. Powell, B.A., et al., *Pu(V) transport through Savannah River Site soils - an evaluation of a conceptual model of surface-mediated reduction to Pu (IV)*. Journal of Environmental Radioactivity, 2014. **131**: p. 47-56.

18. Batuk, O.N., et al., *Multiscale Speciation of U and Pu at Chernobyl, Hanford, Los Alamos, McGuire AFB, Mayak, and Rocky Flats*. Environmental Science & Technology, 2015. **49**(11): p. 6474-6484.
19. Conradson, S.D., et al., *Local and nanoscale structure and speciation in the PuO₂+x-y(OH)(2y)center dot zH(2)O system*. Journal of the American Chemical Society, 2004. **126**(41): p. 13443-13458.
20. EPA, *Method 3052 - Microwave assisted acid digestion of siliceous and organically based matrices*, in *Test methods for evaluating solid waste: Physical/chemical methods*, EPA, Editor. 1996.
21. Jackson, M.L., *Soil Chemical Analysis: Advanced Course*. 1956.
22. Peruski, K., et al., *Determination of constituent concentrations in field lysimeter effluents: FY17 yearly report submitted to Savannah River Remediation in fulfillment of SRRA021685SR*. 2017 Clemson University
23. Powell, B.A., et al., *Stabilization of Plutonium Nano-Colloids by Epitaxial Distortion on Mineral Surfaces*. Environmental Science & Technology, 2011. **45**(7): p. 2698-2703.
24. Kersting, A.B., et al., *Migration of plutonium in ground water at the Nevada Test Site*. Nature, 1999. **397**(6714): p. 56-59.
25. Novikov, A.P., et al., *Colloid transport of plutonium in the far-field of the Mayak Production Association, Russia*. Science, 2006. **314**(5799): p. 638-641.
26. Roberts, K.A., et al., *Characterization of organic-rich colloids from surface and ground waters at the actinide-contaminated Rocky Flats Environmental Technology Site (RFETS), Colorado, USA*. Colloids and Surfaces a-Physicochemical and Engineering Aspects, 2004. **244**(1-3): p. 105-111.
27. Silva, R.J. and H. Nitsche, *Actinide environmental chemistry*. Radiochimica Acta, 1995. **70-1**: p. 377-396.
28. Morse, J.W. and G.R. Choppin, *The Chemistry of Transuranic Elements in Natural-Waters*. Reviews in Aquatic Sciences, 1991. **4**(1): p. 1-22.
29. Kim, J.I., *Chemical Behavior of Transuranic Elements in Natural Aquatic Systems*, in *Handbook on the Physics and Chemistry of the Actinides*, A.J. Freeman and C. Keller, Editors. 1986, Elsevier Science Publishers B. V.
30. Emerson, H.P. and B.A. Powell, *Examination of the Effects of Aging on Desorption and Sorption of Plutonium from 32-year-old Plutonium Contaminated Sediments Using Multiple Isotopes*. Environmental Science and Technology, submitted.