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Analysis of plutonium soil concentrations in field lysimeter experiments: Soil Pu concentration profile from a $\text{NH}_4\text{Pu(V)O}_2\text{CO}_3(\text{s})$ source

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EXECUTIVE SUMMARY

This report describes the analysis of the spatial distribution of a 52 cm long x 10 cm diameter field lysimeter containing an end member soil and a $\text{Pu(V)NH}_4(\text{CO}_3)(\text{s})$ source which was aged in the Savannah River Site, Radionuclide Field Lysimeter Experiments (RadFLEX) for 2 years. The lysimeter was retrieved from the RadFLEX facility and shipped to Clemson University where the lysimeter soil was segmented into 50 sections of approximately 1 cm 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 (2 years, 4 months) compared with previous lysimeter studies (11 years). The downward transport of Pu in the current $\text{Pu(V)NH}_4(\text{CO}_3)$ lysimeter was greater than that observed for previous PuCl_3 , $\text{Pu(NO}_3)_4$, and $\text{Pu(C}_2\text{O}_4)_2$ bearing lysimeters, but almost identical to PuO_2 lysimeter from RadFLEX (Peruski et al., 2017). An 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 $\log K = 3.235 \pm 0.177$ mL/g. 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 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 #41 at the Radiological Field Lysimeter Experiment (RadFLE_x) at the Savannah River Site (SRS). This lysimeter contains a Pu(V)NH₄(CO₃)_(s) source consisting of 80 μCi ²³⁹Pu, 21 μCi ²⁴⁰Pu, and 714 μCi ²⁴¹Pu. The source consists of solid particles of Pu(V)NH₄(CO₃)_(s) sandwiched between two glass fiber filter papers. The filter paper is contained approximately half-way down in a field lysimeter which is 52 cm long x 10 cm diameter and filled with a vadose zone soil from the Savannah River Site. Additional details regarding the RadFLE_x facility are described in the report “SRNL Radionuclide Field Lysimeter Experiment: Baseline Construction and Implementation” by Roberts et al., (Roberts et al., 2012). The RadFLE_x 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 RadFLE_x will complement previously conducted lysimeter experiments (Kaplan et al., 2006a; Kaplan et al., 2014; Kaplan et al., 2004; Kaplan et al., 2007; Kaplan et al., 2006b; Molz et al., 2015), 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 (Demirkanli et al., 2008; Demirkanli et al., 2009; Demirkanli et al., 2007; Kaplan et al., 2006a; Kaplan et al., 2004; Kaplan et al., 2007; Kaplan et al., 2006b). 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 (Hixon et al., 2010; Keeney-Kennicutt and Morse, 1985; Powell et al., 2006; Powell et al., 2004; Powell et al., 2005; Sanchez et al., 1985). 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 (Demirkanli et al., 2008; Demirkanli et al., 2009; Demirkanli et al., 2007). 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 #41 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 (Roberts et al., 2012). Molz et al., (Molz et al., 2015) 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 lysimeter 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 (Powell et al., 2014). 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 (Batuk et al., 2015; Conradson et al., 2004).

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 $\text{Pu(V)NH}_4(\text{CO}_3)_{(s)}$ source bearing lysimeter after 2 years of exposure. 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. These results can be compared with an earlier report from 2017 describing solid phase analysis of Pu from a $\text{PuO}_{2(s)}$ source bearing lysimeter after approximately 3.4 years of exposure to field conditions (Peruski et al., 2017).

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. In the 2017 report, lysimeter #44, $\text{PuO}_2(\text{s})$ source was analyzed. Additionally, Lysimeter 41 ($\text{Pu(V)}\text{NH}_4(\text{CO}_3)$) was removed from RadFLEX in October 16, 2014 and destructively sampled on December 16, 2014. While the segmenting of the lysimeter and soil moisture measurements occurred in 2014, the soil analysis for plutonium concentration and desorption coefficients occurred in 2018, 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).



Figure 1. Photograph of intact soil lysimeter #41 in glove box, after removal of top half of PVC containment.

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 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.

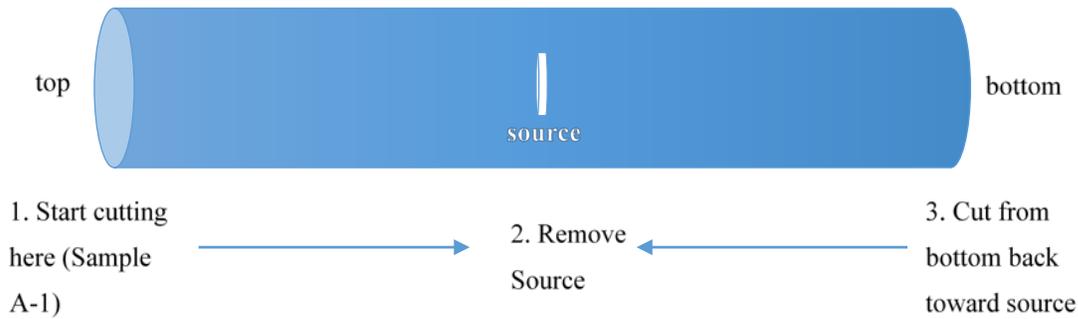


Figure 2: Diagram of sampling procedure

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 soil moisture in the soil sample. After gravimetric determination of water content, dry bulk density of the entire column was calculated and used to convert soil moisture to volumetric water content. Dried soil samples were then placed in Teflon tubes for microwave digestion, and a known activity of ^{242}Pu tracer (0.10 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 (USEPA, 1996).

After microwave digestion, samples were diluted to 8M HNO_3 /0.01M ascorbic acid. Plutonium isotopes were extracted from this solution using extraction chromatography on pre-packed TRU resin columns (Eichrom) with approximately 2 mL bed volumes. Columns were conditioned with 2 column volumes of 8M HNO_3 /0.01M ascorbic acid before sample was added, then washed with 3 more column volumes of 8M HNO_3 /0.01M ascorbic acid afterward. An additional wash step with 3 column volumes of 8M HNO_3 was then performed. Iron was eluted from the column using 1 column volume of 0.01M HNO_3 . Finally, plutonium was eluted from the column using 1 column volume of 0.1M HNO_3 /0.1M oxalic acid solution. The elution was directly analyzed 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 mol_{Pu}/g_{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 between 2.5 cm above and 4.5 cm below the $\text{Pu}(\text{V})\text{NH}_4(\text{CO}_3)$ source. Six locations were chosen in order to evaluate if there is any change with respect to distance from the source, but samples farther than 5 cm below the source could not be analyzed due to insufficient ^{239}Pu activity in sediment. The samples chosen contained between 4 and 67 Bq $^{239}\text{Pu}/\text{g}_{\text{sediment}}$. A 5 g aliquot of pre-homogenized sediment was placed in a 50 mL centrifuge tube containing 50 mL of 10 mM NaCl with triplicate samples prepared for each section. Samples were not pH adjusted but the soil buffering capacity produced a pH of ~5 in all samples. The suspensions were placed on a slow moving platform shaker for 14 days. After 14 days of mixing, the samples were centrifuged to remove particles greater than 100 nm from solution based on Stokes law (Jackson, 1956). The solid and aqueous phases were separated, then a 5mL aliquot of supernatant was taken as the unfiltered solution. Two separate 5mL aliquots of the supernatant were taken for filtration through a 30K MWCO and a 3K MWCO ultrafilter (Microsep Advance Centrifugal device; Pall Corporation). The unfiltered and filtered samples were acidified to 2% HNO_3 for analysis using ICP-MS. Concentration of ^{239}Pu (in parts per billion) was measured on the ICP-MS, then converted to

Bq/mL using the ^{239}Pu half-life of 24,110 years for comparison with the soil concentrations in Bq/g. For each sample, the K_d was calculated by taking the ratio of the Pu concentration in the soil (Bq/g) and in the aqueous phase (Bq/mL) after 14 days of desorption. A second sampling of the desorption experiment was taken after 8 weeks and sampled in the same manner as the 14-day sampling event.

4. Results & Discussion

The soil and source material were all successfully removed and separated during coring. 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 41 ranged from 22-29% (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.

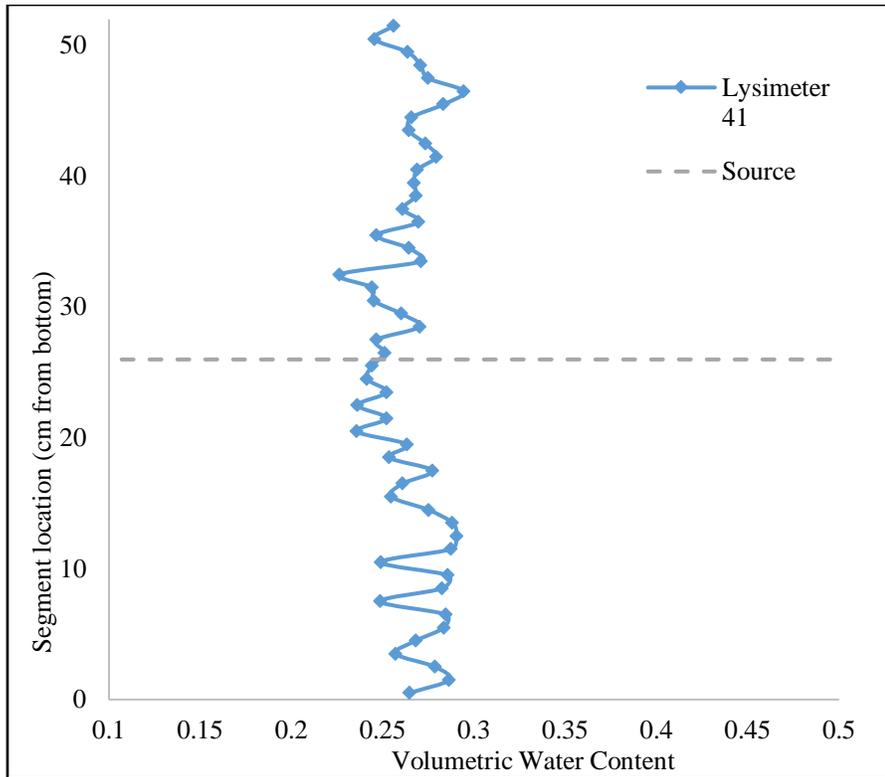


Figure 4: Volumetric water content as a function of location in the lysimeter, where 0 is the base of the lysimeter and 49 cm is the top. Source is located at 26 cm.

Plutonium Lysimeter Soil Analysis

Soil digestions and ion exchange had an average chemical yield for ^{242}Pu of 17.3%. 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 ^{239}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 2. An example calibration curve for ICP-MS determination of ^{239}Pu is shown in the Appendix (Figure A1). The ICP-MS detection limit was 7.0×10^{-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 $[^{239}\text{Pu}]_{DL,ICPMS}$ is the ICPMS detection limit.

$$^{239}\text{Pu} - \text{MDC} = \frac{[^{239}\text{Pu}]_{DL,ICPMS} * V_{ICPMS}}{\frac{Y}{m_{soil}}} \quad \text{Equation 2.}$$

The MDC was 9.35×10^{-4} Bq/g and all positive measurements of ^{239}Pu were at least one order of magnitude above the detection limit.

^{239}Pu transport was observed greater than 14 cm below source, with maximum concentrations at approximately 67 Bq/g (Figure 5). Above source, ^{239}Pu is measured up to 4 cm above source, but quickly dropped below detection limits. Two data points exist at 9.5 cm and 16.5 cm above the source showing measurable ^{239}Pu , where all points surrounding have no measurable ^{239}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 base of the lysimeter contains measurable ^{239}Pu , 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 (Peruski et al., 2017), indicating that Pu has moved to the base of the lysimeter. (Figure 5).

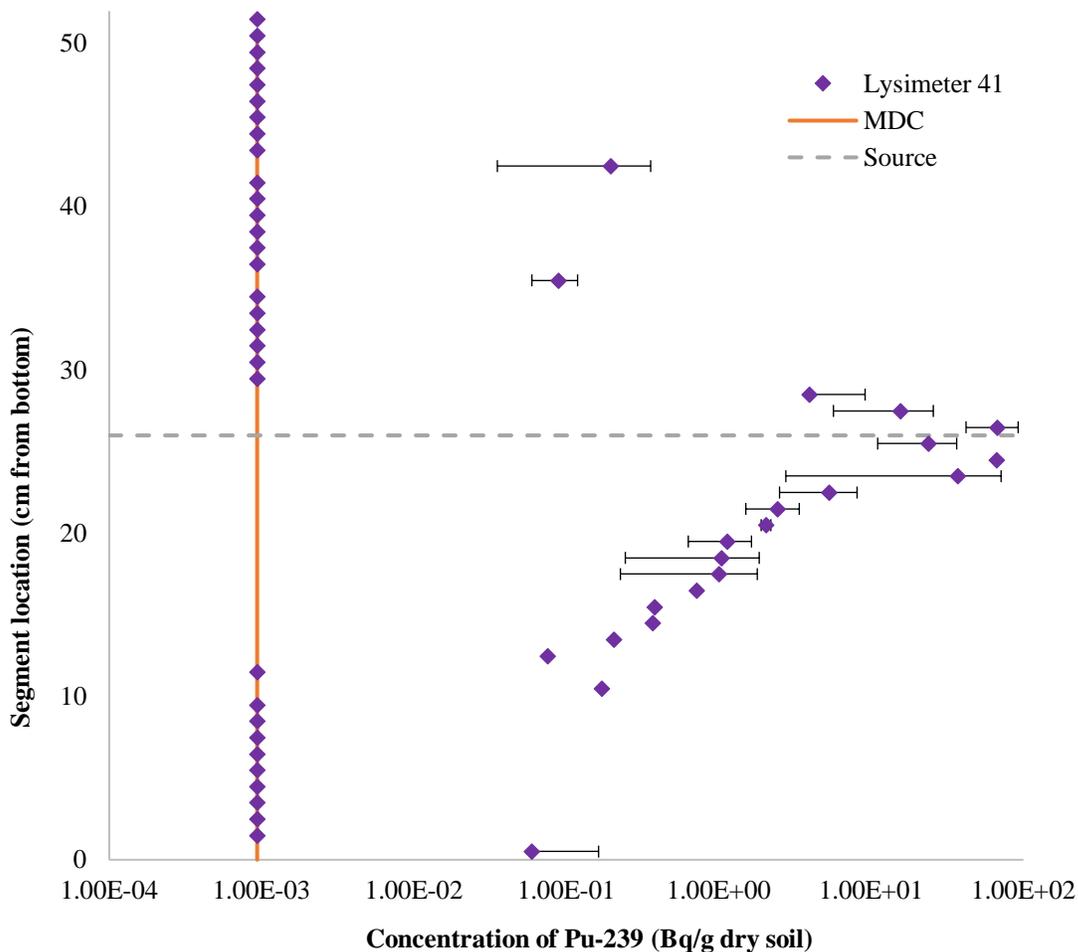


Figure 5. ²³⁹Pu concentration (in Bq/g) for Lysimeter 41 soil samples as a function of location in the lysimeter, where 0 cm is the base and 52 cm is the top. Standard deviation calculated from standard deviation of ICP-MS measurements. MDC= minimum detectable concentration, calculated from ICP-MS measurements.

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 Pu(V)NH₄(CO₃) lysimeter analyzed in this work (purple markers in Figure 6) shows slightly enhanced transport (an increase of a few cm) below the source as compared to the older Pu lysimeters, but is almost identical to transport from the PuO₂ lysimeter analyzed in 2017. Upward transport from the Pu(V)NH₄(CO₃) lysimeter is less than the older Pu lysimeters, but similar to the PuO₂ lysimeter. Assuming that the upward migration near the source was due to diffusion, the slight decrease in upward transport was likely due to the shorter time in the field (2-3 years) relative to the other lysimeters (11 years) (Kaplan et al., 2006a; Kaplan et al., 2004; Kaplan et al., 2007). Without further modeling analysis, it is difficult to determine if the observation of greater downward

migration of Pu in recent lysimeters is significant. It is assumed that a similar oxidation-reduction process will control the migration of Pu within lysimeters. As discussed above, formation of PuO_2 from all Pu source 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 similarity in transport from $\text{Pu(V)NH}_4(\text{CO}_3)$ and PuO_2 suggest that Pu transport may be independent of source material. A working hypothesis is that transformation of source material to a disordered PuO_2 phase occurs quickly, before significant dissolution and transport of the source material can occur, especially considering dissolution is slow and transport is highly retarded in the sediment, thus leading to similar transport from different sources. Further

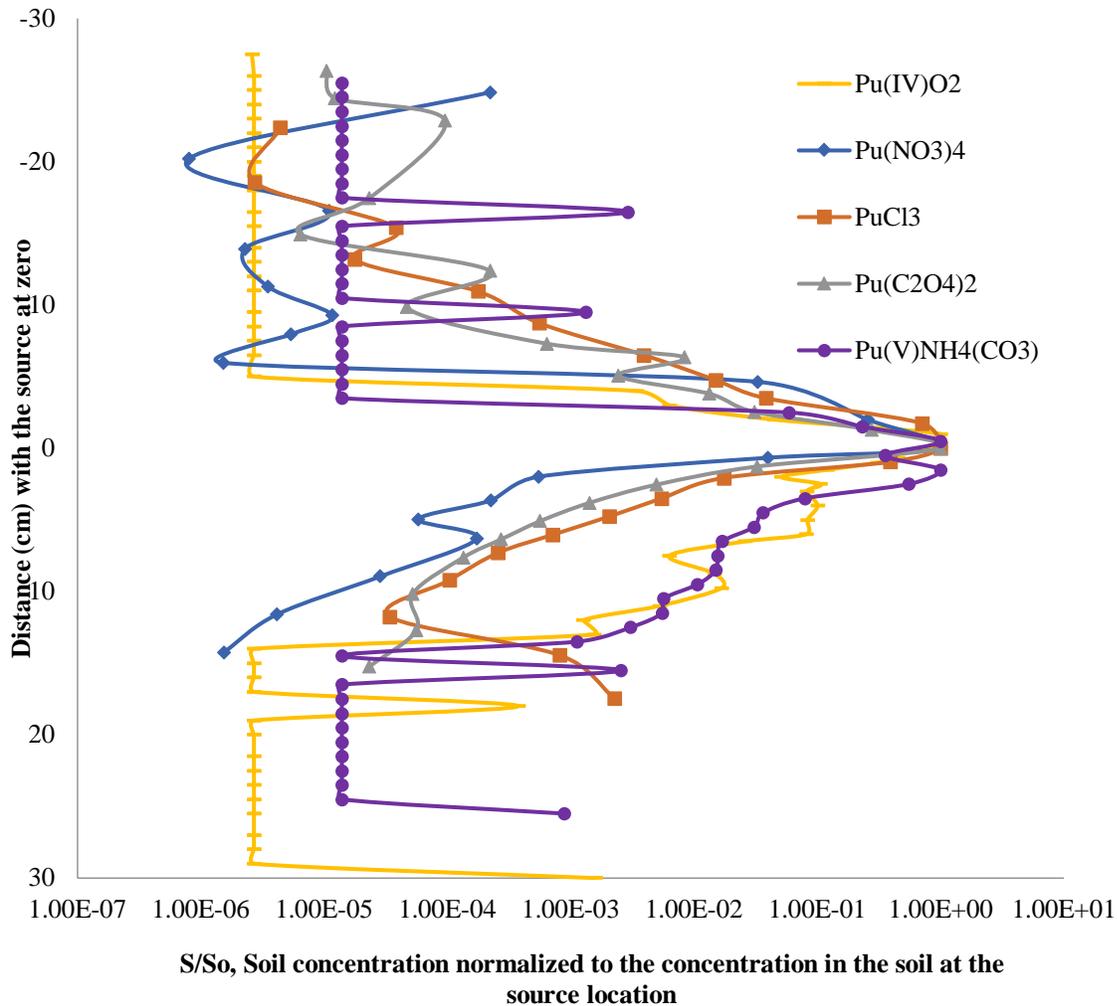


Figure 6. Comparison of Pu transport from lysimeters of varying Pu source material. Concentrations are normalized to the maximum concentration at the source region. Data for $\text{Pu(NO}_3)_4$, PuCl_3 , and $\text{Pu(C}_2\text{O}_4)_2$ lysimeters from (Kaplan et al., 2006a; Kaplan et al., 2004; Kaplan et al., 2007).

processing of other Pu lysimeters from RadFLEx, each with different source materials, will provide further insight into this hypothesis.

Batch desorption experiments

Presence of Pu 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.

Desorption K_d values ranged from 900-2400 mL/g (Figure 7), showing no apparent difference between filtered or unfiltered samples. This indicates that colloid transport is not a significant factor in the $\text{Pu(V)NH}_4(\text{CO}_3)$ source lysimeter. The average log K_d value for all soils analyzed is 3.23 ± 0.18 mL/g. 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. (Emerson and Powell, 2018).

However, there was no apparent difference between the desorption K_d values from samples above or below the immediate source region, and no significant difference in values as a function of distance from source. Though only supported by indirect evidence, this would indicate that the chemical species of Pu associated with the soil is the same throughout 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.

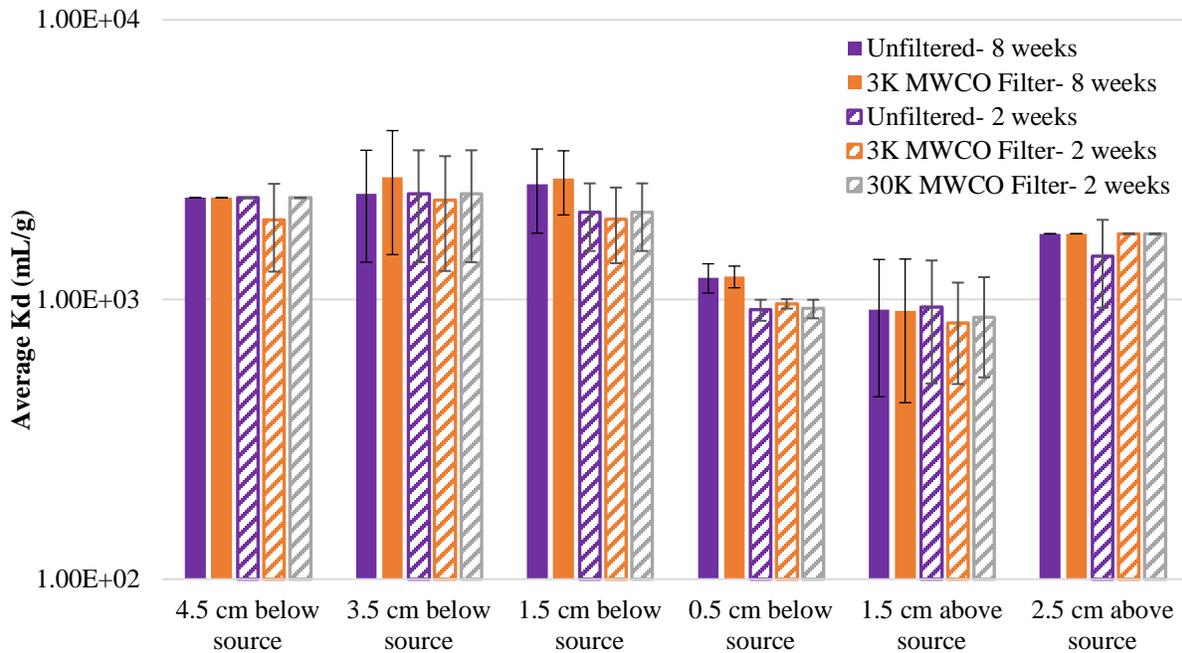


Figure 7: Calculated desorption conditional K_d values from desorption experiments with soils from near the source region of lysimeter 41. Data obtained after 2 weeks and 8 weeks of equilibrium, with standard deviation representing triplicate samples.

5. Summary

Analysis of lysimeter 41 containing a $\text{Pu(V)NH}_4(\text{CO}_3)$ source indicated both downward as well as a slight upward migration of Pu. The upward migration of Pu was decreased relative to older lysimeters, but similar to the PuO_2 lysimeter analyzed in 2017. This difference is proposed to be due to the shorter deployment time of the current lysimeter (2-4 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 $\text{Pu(V)NH}_4(\text{CO}_3)$ lysimeter is almost the same as the PuO_2 lysimeter, but was greater than that observed for previous PuCl_3 , $\text{Pu(NO}_3)_4$, and $\text{Pu(C}_2\text{O}_4)_2$ bearing lysimeters. Similarity between $\text{Pu(V)NH}_4(\text{CO}_3)$ and PuO_2 lysimeter transport may be attributed to the transformation of source materials to a similar PuO_2 phase, which occurs on a scale far more rapid than transport. The potential formation of PuO_2 -colloids which could cause the greater downward movement of Pu in lysimeters 41 and 44, needs to be examined further.

Desorption experiments using Pu contaminated soils retrieved from this lysimeter indicated desorption distribution coefficients with $\log K_d = 3.24 \pm 0.18$ mL/g. There was no

apparent difference between unfiltered and filtered 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 PuO₂ colloids to iron oxide surfaces (Powell et al., 2011). 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 41

Sample ID	Location (cm) from bottom	Mass of wet soil (g)
41-T-1	51.5	162.48
41-T-2	50.5	117.36
41-T-3	49.5	135.51
41-T-4	48.5	209.38
41-T-5	47.5	113.67
41-T-6	46.5	206.02
41-T-7	45.5	132.69
41-T-8	44.5	148.07
41-T-9	43.5	185.29
41-T-10	42.5	141.59
41-T-11	41.5	157.65
41-T-12	40.5	134.81
41-T-13	39.5	144.56
41-T-14	38.5	174.67
41-T-15	37.5	145.4
41-T-16	36.5	145.39
41-T-17	35.5	135.36
41-T-18	34.5	142.75
41-T-19	33.5	144.36
41-T-20	32.5	137.9
41-T-21	31.5	160.19
41-T-22	30.5	149.57
41-T-23	29.5	66.14
41-T-24	28.5	165.19
41-T-25	27.5	143.38
41-B-27	26.5	135.58
41-B-26	25.5	86.5
41-B-25	24.5	35.7
41-B-24	23.5	196.54
41-B-23	22.5	131.4
41-B-22	21.5	126.8
41-B-21	20.5	164.16
41-B-20	19.5	113.35
41-B-19	18.5	97.53

Sample ID	Location (cm) from bottom	Mass of wet soil (g)
41-B-18	17.5	138.57
41-B-17	16.5	153.13
41-B-16	15.5	146.72
41-B-15	14.5	164.54
41-B-14	13.5	159.27
41-B-13	12.5	145.76
41-B-12	11.5	138.78
41-B-11	10.5	99.05
41-B-10	9.5	164.39
41-B-9	8.5	122.3
41-B-8	7.5	125.74
41-B-7	6.5	151.62
41-B-6	5.5	166.62
41-B-5	4.5	157.92
41-B-4	3.5	160.91
41-B-3	2.5	110.7
41-B-2	1.5	105.01
41-B-1	0.5	144.29

Table A2. Volumetric water content data for lysimeter 41

Sample ID	Segment Location (cm from bottom)	Volumetric Water Content (cm³ water per cm³ soil)
41-T-1	51.5	0.25585054
41-T-2	50.5	0.24536267
41-T-3	49.5	0.26351042
41-T-4	48.5	0.27069473
41-T-5	47.5	0.27485265
41-T-6	46.5	0.29449383
41-T-7	45.5	0.2833582
41-T-8	44.5	0.26591872
41-T-9	43.5	0.26436172
41-T-10	42.5	0.27334943
41-T-11	41.5	0.27940173
41-T-12	40.5	0.26894905
41-T-13	39.5	0.26718446
41-T-14	38.5	0.26807741
41-T-15	37.5	0.26102499
41-T-16	36.5	0.26956573
41-T-17	35.5	0.24672912
41-T-18	34.5	0.26428937
41-T-19	33.5	0.27106174
41-T-20	32.5	0.22647102
41-T-21	31.5	0.24410983
41-T-22	30.5	0.24504162
41-T-23	29.5	0.26002431
41-T-24	28.5	0.27012111
41-T-25	27.5	0.24654644
41-B-27	26.5	0.25103774
41-B-26	25.5	0.24408014
41-B-25	24.5	0.24136682
41-B-24	23.5	0.25225294
41-B-23	22.5	0.23622242
41-B-22	21.5	0.25220615
41-B-21	20.5	0.23567985
41-B-20	19.5	0.26322911
41-B-19	18.5	0.25365205
41-B-18	17.5	0.27725044
41-B-17	16.5	0.26071178

Sample ID	Segment Location (cm from bottom)	Volumetric Water Content (cm³ water per cm³ soil)
41-B-16	15.5	0.25474654
41-B-15	14.5	0.27502999
41-B-14	13.5	0.28815029
41-B-13	12.5	0.29037002
41-B-12	11.5	0.28742784
41-B-11	10.5	0.24901555
41-B-10	9.5	0.28558237
41-B-9	8.5	0.28257124
41-B-8	7.5	0.24851225
41-B-7	6.5	0.2845727
41-B-6	5.5	0.28351672
41-B-5	4.5	0.26813298
41-B-4	3.5	0.25709444
41-B-3	2.5	0.27870437
41-B-2	1.5	0.28640628
41-B-1	0.5	0.26468897

Table A3. ²³⁹Pu concentration (in Bq/g) for lysimeter 41 soil samples. Standard deviation calculated from standard deviation of ICP-MS measurements. MDC= minimum detectable concentration, calculated from ICP-MS measurements equal to 9.35×10^{-4} Bq/g..

Sample ID	Bq Pu-239/g dry soil	Standard Deviation (Bq/g)	Segment Location (cm from bottom)
41-T-1	0	0	51.5
41-T-2	0	0	50.5
41-T-3	0	0	49.5
41-T-4	0	0	48.5
41-T-5	0	0	47.5
41-T-6	0	0	46.5
41-T-7	0	0	45.5
41-T-8	0	0	44.5
41-T-9	0	0	43.5
41-T-10	0.19646136	0.16121922	42.5
41-T-11	0	0	41.5
41-T-12	0	0	40.5
41-T-13	0	0	39.5
41-T-14	0	0	38.5
41-T-15	0	0	37.5
41-T-16	0	0	36.5
41-T-17	0.08896199	0.02954238	35.5
41-T-18	0	0	34.5
41-T-19	0	0	33.5
41-T-20	0	0	32.5
41-T-21	0	0	31.5
41-T-22	0	0	30.5
41-T-23	0	0	29.5
41-T-24	3.94275741	5.19976301	28.5
41-T-25	15.6333902	9.96956774	27.5
41-B-27	67.1907086	25.1682004	26.5
41-B-26	23.7690259	12.7175463	25.5
41-B-25	66.9577103	29.74655738	24.5
41-B-24	37.0671214	34.3093167	23.5
41-B-23	5.30140034	2.79354801	22.5
41-B-22	2.44286642	0.93591404	21.5
41-B-21	2.04900477	0.15010496	20.5
41-B-20	1.13628379	0.50458857	19.5
41-B-19	1.04390281	0.80006512	18.5

Sample ID	Bq Pu-239/g dry soil	Standard Deviation (Bq/g)	Segment Location (cm from bottom)
41-B-18	1.00884408	0.78248768	17.5
41-B-17	0.71813139	0	16.5
41-B-16	0.38114044	0	15.5
41-B-15	0.37117044	0	14.5
41-B-14	0.20501188	0	13.5
41-B-13	0.07534217	0	12.5
41-B-12	0	0	11.5
41-B-11	0.17082861	0	10.5
41-B-10	0	0	9.5
41-B-9	0	0	8.5
41-B-8	0	0	7.5
41-B-7	0	0	6.5
41-B-6	0	0	5.5
41-B-5	0	0	4.5
41-B-4	0	0	3.5
41-B-3	0	0	2.5
41-B-2	0	0	1.5
41-B-1	0.05957995	0.10319549	0.5

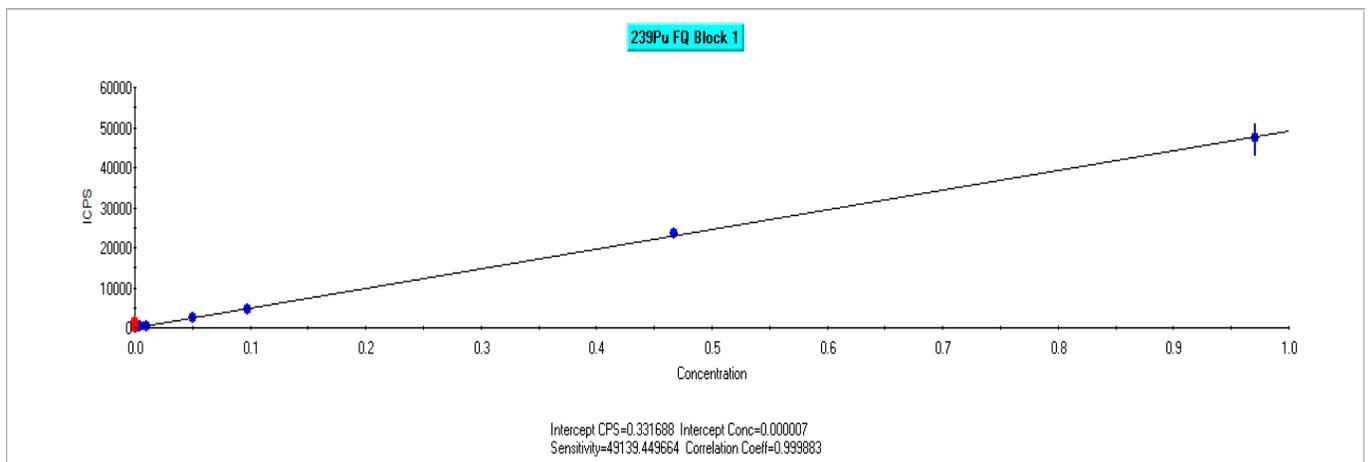


Figure A1: ICPMS calibration curve for ²³⁹Pu. Thermo X Series II ICPMS

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