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Upward Movement of Plutonium to Surface Sediments During an 11-Year Field Study

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Abstract

An 11-y lysimeter study was established to monitor the movement of Pu through vadose zone sediments. Sediment Pu concentrations as a function of depth indicated that some Pu moved upward from the buried source material. Subsequent numerical modeling suggested that the upward movement was largely the result of invading grasses taking up the Pu and translocating it upward. The objective of this study was to determine if the Pu of surface sediments originated from atmosphere fallout or from the buried lysimeter source material (weapons-grade Pu), providing additional evidence that plants were involved in the upward migration of Pu. The $^{240}Pu/^{239}Pu$ and $^{242}Pu/^{239}Pu$ atomic fraction ratios of the lysimeter surface sediments, as determined by Thermal Ionization Mass Spectroscopy (TIMS), were 0.063 and 0.00045, respectively; consistent with the signatures of the weapons-grade Pu. Our numerical simulations indicate that because plants create a large water flux, small concentrations over multiple years may result in a measurable accumulation of Pu on the ground surface. These results may have implications on the conceptual model for calculating risk associated with long-term stewardship and monitored natural attenuation management of Pu contaminated subsurface and surface sediments.

1. Introduction

The long-term behavior of Pu in the environment is becoming increasingly important as we enter into new phases of the lifecycle of Pu: disposal, recycling into fuel, and remediation of Pu contaminated environments. Plutonium in high-level waste tanks is being vitrified and will be eventually disposed in a deep national repository. Plutonium in low-level waste is being disposed at various shallow vadose-zone facilities. Some pure forms of Pu will be recycled by converting into mixed oxide fuels (or MOX) for use in electrical nuclear power plants. During the production of Pu between the 1950s through the 1980s environmental contamination occurred at several Department of Energy sites, including Los Alamos National Laboratory, Hanford Site, Idaho National Laboratory, Oak Ridge National Laboratory, and the Savannah River Site (Riley and Zachara, 1992). These Pu-contaminated sites have been or will be remediated. In some cases, contaminated sediments have been excavated and treated elsewhere, whereas at other contaminated sites, amendments are mixed into the sediment to reduce the bioavailability or movement of the Pu. But perhaps most commonly, sites contaminated with low concentrations of Pu will be left intact and its movement will be monitored through a long-term monitoring and natural attenuation plan. In all three remediation approaches, some Pu will be left in the ground, and the management of Pu in the environment must be based on sound, long-term science.

Four lysimeters were established on the Savannah River Site (SRS) located in Aiken, South Carolina, USA to evaluate the long-term transport of Pu through vadose zone sediments (described in Kaplan et al., 2004; 2006; 2007). The lysimeters consisted of inverted 52-L bottomless carboys that were connected to separate leachate collection reservoirs. The lysimeters were filled with well-mixed subsurface sediment and amended with approximately 1.7

x 10^7 Bq (3.4 x 10^{-5} mol) of Pu, added as $Pu^{IV}(NO_3)_4$, $Pu^{IV}(C_2O_4)_2$, $Pu^{III}Cl_3$, or $Pu(OH)_4$. The Pu sources existed as solids and were placed 22 cm below the surface. The lysimeters were initiated in 1981 and were exposed to natural weather conditions (average = 122 cm y^{-1} precipitation) for 11 years. The test plan called for grass (weeds) found growing in the lysimeters to be cut and the biomass left on the lysimeter surface (avoiding a potential radioactive waste disposal problem). Vertical sediment cores were collected from the center of the lysimeters and then these cores were cut up into 1.25- or 2.5-cm thick depth-discrete samples. Total $^{239/240}Pu$ concentrations were measured by alpha spectrometry in each sample.

Sediment cores recovered from these lysimeters reveled that a significant portion of the Pu moved upward (Figure 1). Pu downward movement was well described by a fully transient reactive transport model that took into consideration transient sediment moisture saturation, steady state Pu sorption, and kinetic terms to describe Pu(IV) oxidation to Pu(V) and Pu(V) reduction to Pu(IV) (Demirkanli et al., 2007). However, this same model could not describe Pu upward movement (Demirkanli et al., 2008). For a range of sediment properties, these simulations showed that the upward soil water flux due to evapotranspiration, which accounted for about 1/2 to 2/3 of the water that entered the lysimeters, was not sufficient to explain the observed upward movement of Pu. Further computer testing permitted us to eliminate several other potential chemical and hydraulic processes, including one in which Pu became more oxidized (and mobile) as the sediment's moisture-content decreased; adjusting the hypothetical root-distribution to favor upward fluxes of water; and considering hysteresis, caused higher hydraulic conductivities in the sediment for a drying condition than a wetting condition. Following these studies, Demirkanli et al. (2009) concluded that the upward movement of Pu was the likely result of Pu root uptake and translocation within the transpiration (xylem) pathway.

This conclusion was based on computer simulations that produced successful modeling of Pu xylem transport using physically meaningful plant and sediment parameters.

In two of the three Pu core profiles, the profiles amended with $Pu(NO_3)_4$ and $PuCl_3$, a slight increase in sediment Pu concentrations were noted in the surface 2.5-cm thick samples (Figure 1). This increase in surface sediment Pu concentrations could be attributed to either atmospheric deposition, or to plant material depositing Pu to the surface sediment as a result of annual die back. If the latter was true, then it would provide direct evidence in support of the conclusion by Demirkanli et al. (2009) that Pu upward movement was due to plant uptake and subsequent redistribution in the sediment profile. Another possibility was that earthworms were responsible for the upward Pu movement. We ruled out bio-perturbation, such as earthworm activity, based on two observations: 1) after careful inspection, no earthworm galleys or other animal activities were found in the sediment cores, and 2) the shape of the Pu depth profiles in Figure 1 were not like those of a bio-perturbed system. Bio-perturbed systems characteristically show the surface sediment layers with an erratic concentration profile down to the depth where the worms exist. These Pu concentration profiles, especially for the $PuCl_3$ and $Pu(C_2O_4)_2$, show a rather symmetrical shape above and below the source, with most of the scatter of the data occurring at low sediment-Pu concentrations.

1.1 Plant Uptake

Plutonium exists in four oxidation states in the natural environment, +3, +4, +5 and +6 (Silva and Nitsche, 1995). The oxidized forms are appreciably more soluble and mobile in sediments than the reduced forms. Pu(V) and Pu(VI) have been shown to undergo rapid reduction by numerous mineral surfaces. Thus, most of the Pu in sediments exists in the reduced form, even

in surface sediments with seemingly oxidizing conditions (Powell et al. 2005). Plant uptake of sediment Pu is extremely limited with surprisingly similar concentration ratios (ratio of the concentration in above-ground plant to the concentration in sediment) reported in the literature, ranging from 10^{-5} to 10^{-4} for a wide range of plants and sediments [reviewed by Wang et al., 1993).

Cataldo et al. (1988) reported that Pu in the xylem of soybean plants (Glycine max (L.)) existed almost exclusively as an organic complex. Pu^{+4} in the uncomplexed form was immediately and strongly retained by the xylem and did not translocate within the plant. Wildung and Garland (1974) observed from autoradiographs of barley (Hordeum vulgare var. Vangard) that Pu was evenly distributed within the roots and tended to concentrate in the crown. They concluded that although Pu may be strongly bound to sediments, the little amount of Pu that entered the plant was readily distributed through the root system as an organo-Pu complex, moving both upward and downward in the root profile. Furthermore, they concluded that the potential exists for decomposing roots to be a significant source of Pu of different solubility than the Pu that originally entered the soil environment. It is possible that the observed increases of Pu uptake with successive plantings of clover during a 10 year field study resulted from this latter phenomenon (Romney et al., 1970).

Plants have been shown to enhance sediment metal and radionuclide bioavailability through the release of root exudates, including phytosideraphores (Bais et al., 2006; Rengel and Romheld, 2000) and release of siderophores from root-associated microbes (Bar-Ness et al., 1992). The presence of these plant-derived organic molecules can behave as ligands, increasing Pu solubility, especially for Pu(III) and Pu(IV). Additionally, microbial populations increase in the rhizosphere, the organic carbon rich root environment, and play important direct (metabolize) or

132 indirect (release of extracellular polymeric substances) roles influencing metal/radionuclide
133 phytoavailability.

134 There are very few examples in the literature of clearly documented upward movement of
135 radionuclides in systems where the net movement of soil water is downward. Sanford et al.
136 (1998) reported that Cs and Sr may have moved upward 100 cm during a 10 year field lysimeter
137 study conducted at the Oak Ridge National Laboratory. In a recovered vertical sand core, they
138 observed a root of an unidentified plant. The root had ^{137}Cs concentrations that were about 1.5
139 orders-of-magnitude greater than the bulk sand concentrations. The sand ^{137}Cs concentrations
140 decreased sharply away from the root. They concluded that the root was responsible for the
141 observed upward movement of ^{137}Cs.

142

143 **1.2 Atmospheric deposition of plutonium**

144 Plutonium originating from atmospheric nuclear weapons testing is the largest source of Pu
145 to the environment and can be detected throughout the earth's surface, with the greatest
146 concentration existing in the northern hemisphere and the lowest in Antarctica (Harley 1980;
147 Perkins and Thomas, 1980). Differences in weapons design and yield account for much of the
148 variability measured in the ^{240}Pu/^{239}Pu isotopic ratios of fallout Pu (Perkins and Thomas, 1980).
149 For example, the average global fallout ^{240}Pu/^{239}Pu ratio is 0.18, where the ratio from the Nevada
150 Test Site is generally lower, averaging 0.035. Higher ratios can be generally expected with the
151 higher neutron fluxes associated with an increase in the yield of a nuclear detonation, and will
152 vary with weapons design. Such elevated ratios have been measured in environmental samples
153 impacted by nuclear weapons testing in the Pacific (Koide et al., 1983). Therefore, the relative
154 abundances of ^{239}Pu, ^{240}Pu, and other minor Pu isotopes such as ^{241}Pu and ^{242}Pu can be used to

trace the specific Pu source because Pu isotopic ratios can vary with reactor type, nuclear fuel burn-up time, and neutron flux and energy (Beasley et al., 1981; Buesseler, 1997).

The hypothesis of the present study is that the surface accumulation of Pu was the result of Pu being taken up by plant roots, translocated to the above-ground portion of the plants, and then deposited as plant detritus on the ground surface. This hypothesis was prompted by three observations: 1) elevated total Pu concentrations in some surface sediment samples collected at the lysimeter, 2) the intermittent presence of grasses growing on the lysimeters (Andropogon virginicus, broomsedge; Paspalum notatum, Bahia grass; and Digitaria sp., crabgrass), and 3) modeling results (Demirkanli et al. (2009) suggesting that a substantial amount of Pu could be taken up by lysimeter plants during the 11 year experiment. Thus, the objective of this study was to determine whether the source for the Pu in the surface sediment samples was from atmospheric deposition or the underlying weapons-grade Pu materials added to each lysimeter. Our approach was to compare Pu isotopic ratios of the lysimeter surface sediments with those of two types of controls: a positive control for the weapons-grade Pu buried in the lysimeters (a lysimeter sediment sample collected from within 6 cm of the $Pu^{IV}(NO_3)_4$ buried source material), and two positive controls for atmospheric deposition. Plutonium isotopic ratios were determined by thermal ionization mass spectroscopy (TIMS), an extremely sensitive method for detecting isotopes with detection limits in the order of 0.2 fg g^{-1} ^{239}Pu or 8 x 10^{-19} mole g^{-1} ^{239}Pu. Such low detection limits are the result of including several internal analytical sample controls, using large volumes of sample (up to 20 g per sample for the fallout control samples in this study), the use of a sensitive instrument housed in a Class 10,000 clean room, and perhaps most importantly final sample loading in a Class 1000 hood. In addition to conducting TIMS analyses, we also conducted numerical simulations to describe the impact that plants may have on Pu

concentrations in a lysimeter sediment profile. The model was also used to predict Pu uptake by lysimeter grasses and subsequent distribution within roots and transfer into shoots over the duration of the lysimeter experiment, 11 years.

2. Materials and methods

2.1 Sediment samples

A total of seven sediment samples were analyzed by TIMS for ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{242}Pu: four lysimeter surface sediments, one positive control for the weapons-grade Pu, and two positive controls for atmospheric fallout. The two fallout control samples were expected to contain varying Pu isotopic ratios by virtue of their varying distance from the SRS, a former weapons production facility: one sample was collected on the Savannah River Site perimeter, 16 km from the lysimeter field site, and the second sample was collected from Anderson, South Carolina, USA 190 km from the lysimeter field site. The positive control for the weapons-grade Pu, the Pu source material buried in the four lysimeters, was collected 6 cm below the $Pu^{IV}(NO_3)_4$ source; it contained 14.15 Bq g^{-1} $^{239/240}$Pu and 0.25 Bq g^{-1} ^{238}Pu. Prior to preparing the sediments for TIMS analysis, the visible organic matter, including forest litter and roots, was removed from the fallout control samples. No organic matter was visibly present in the other five samples. All samples were passed through a 2-mm sieve.

The lysimeter sediment has been described previously (Kaplan et al., 2004). Briefly, it has a sandy loam texture, a 1:1 sediment:water pH of 6.3, and no measurable organic matter. Its red color is derived from the high concentration of iron-(oxy)hydroxides, especially hematite, which showed a strong presence in X-ray diffraction and Mössbauer measurements. The high total Fe

concentrations (15,888 mg kg^{-1}) and low Fe(II) / Fe(III) ratios (1.9% / 98.1%) are typical of vadose zone sediments of this region. In apparent contradiction with the oxidizing nature of the Fe-oxyhydroxides, this sediment can quickly reduce Pu(V) to Pu(IV) (Kaplan et al., 2004). Sediment Mn concentrations, a potential oxidizing or reducing agent, are low at about 630 mg kg^{-1}.

2.2 Thermal Ionization Mass Spectroscopy Analyses (TIMS)

A description of the sample preparation protocol is presented in Landa et al. (1998) and a description of the TIMS instrument is presented in Halverson (1981) and Buesseler and Halverson (1987). A 1 to 20 g sediment sample was analyzed. A 0.002 Bq (0.06 pCi) aliquot of ^{242}Pu was added to some of the samples (the two fallout control samples) to provide an internal standard for quantifying Pu isotope concentrations by mass spectroscopy. However, ^{242}Pu was not added to all samples because ^{242}Pu/^{239}Pu atomic mass ratios were of interest. Quantification of $^{239/240}$Pu and ^{238}Pu concentrations was provided by alpha spectrometry analyses on a separate aliquot. The samples were then leached with hot 8 M nitric acid and hydrogen peroxide for several hours. The slurry was transferred to a centrifuge tube and the undigested residue separated from the supernate. The supernate was taken to near dryness and then diluted with deionized water. Initial separation from the matrix ions and U was achieved by precipitating hydroxides of iron from a carbonate rich solution; ammonium hydroxide was added to the solution until a pH of about 5, and then a saturated solution of ammonium carbonate was added to a pH of 8. The precipitate with entrained Pu was separated by centrifugation and the supernate discarded.

223 Several ion exchange separation columns were used to purify the Pu prior to mass
224 spectrometry analysis. For the first column separation, the Pu was reduced to the +4 oxidation
225 state using $NaNO_2$ in 8 M nitric acid and then recovered with a 20 mL column using an 8%
226 cross-linked anion exchange resin (AG 1X8). Interfering elements were washed through the
227 column and the Pu finally eluted after reduction to the +3 state with NH_4I/HCl. The eluant
228 containing the Pu was taken to dryness, converted to the +4 oxidation state and passed through a
229 5 mL bed volume, 4% cross-linked, anion exchange column (AG 1X4). The column purification
230 was repeated once more using only a 0.5 mL bed volume of the 4% cross-linked resin, using HBr
231 to ultimately elute the Pu. This final purified sample was then analyzed by TIMS.
232 Plutonium was sorbed onto a few resin beads which were then mounted onto a canoe shaped
233 rhenium- ribbon filament for the instrumental analysis. The three-stage TIMS analyzer
234 (Halverson, 1987) was used for the analysis rather than the single-sector TIMS analyzer (Landa
235 et al., 1998) in order to provide values for the Pu isotopes of lower abundance, ^{241}Pu and ^{242}Pu.
236 The three-sector TIMS analyzer consists of two identical magnetic analyzers in a C-
237 configuration followed by an electrostatic analyzer and an ion-multiplier type detector. As noted
238 above, this instrument is housed in a Class 10,000 clean-room facility. Filament fabrication and
239 sample loading is performed in laminar flow hoods rated at Class 1000.
240 Typical recoveries for the analysis of Pu in soil and sediment by this procedure average
241 between 75 to 90% as determined by the analysis of the ^{242}Pu spiked samples. Calculated
242 detection limits are on the order of 0.2 fg/g (0.5μBq/g) for ^{239}Pu, based on the analysis of reagent
243 blanks. The NIST Columbia River sediment (SRM 4334G) was used as a Quality Control
244 samples for accuracy and precision. The NIST Columbia River sediment is certified for 7.6 ±
245 2.1 Bq g^{-1} $^{239/240}$Pu and we measured 6.6 ± 2.0 Bq g^{-1} $^{239/240}$Pu (Cadieux et al., 2007). The

reagent blank had a trace of $^{239/240}Pu$ activity, indicating some cross contamination of samples. This slight contamination did not compromise data interpretation.

2.3 Numerical Model

A numerical model was used to describe the long term impact that plants may have on Pu concentrations in a lysimeter sediment profile. The model was also used to predict Pu uptake and distribution within the plant (root and shoots). The model included yearly decay of the roots, allowing Pu activity in the root to be transferred back into the sediments at the end of each year. A detailed description of the numerical model is presented in Demirkanli et al. (2007; 2008; 2009). We used this existing model for hypothesis testing. Briefly, the fully transient reactive transport modeling of Pu consists of three models, all time-dependent and coupled to each other through various parameters: (1) a variably saturated flow model; (2) a reactive Pu sediment transport model; and (3) a Pu root uptake and xylem transport model. The flow model simulates the time-dependent moisture movement within the sediment core depending on: (1) the daily rainfall data collected during the experiments; (2) root water uptake calculated based on the average monthly temperature; and (3) measured and inferred sediment hydraulic characteristics. The output values of parameters, the velocity and moisture content, for a given time and location within the core are then transferred into the reactive transport model to calculate the Pu movement in the soil core due to reaction, advection, and dispersion. The geochemical processes described by the transport model included two Pu species: a reduced species, Pu(III/IV), and an oxidized species, Pu(V/VI). Kinetic reaction terms were used to describe Pu oxidation and reduction reactions occurring on sediment surfaces. Rate constants for these reactions were used as fitting parameters. Pu(III/IV) and Pu(V/VI) were also assumed to partition to the solid phase

using steady-state equilibrium constants. The calculated root water uptake term from the flow model and sediment solution Pu activity concentrations from the reactive transport model were used in the Pu root uptake and transport model to simulate the uptake and Pu transport within the xylem. Pu transport within the xylem occurred by advection and dispersion assuming that the aqueous phase Pu(III/IV) and Pu(V/VI) were transferred into the plant with water uptake. Radial passage between the root-sediment interface and the xylem was assumed to be instantaneous with no sorption to plant material. However, after moving into the xylem, Pu was assumed to sorb onto the xylem wall material of the roots, mainly cellulose, consequently causing retardation. Pu leaving the domain through the top boundary of the root model, i.e., the lysimeter sediment surface, was assumed to be transferred into the above-ground part of the plants (shoots). Yearly senescence of shoots was not included in the initial model.

3. Results and discussion

3.1. Plutonium isotopes

Plutonium sediment concentrations and atomic mass fractions of Pu isotopes are presented in Table 1. Not surprisingly, ^{239,240}Pu concentrations were greater than ^{238}Pu. The weapons-grade Pu control sample had about three orders of magnitude greater ^{239,240}Pu concentrations than did the lysimeter surface sediments, except for the surface $Pu(NO_3)_4$ sample. The two positive controls for fallout also had low Pu concentrations. ^{239}Pu and ^{240}Pu, the isotopes with the greatest mass fractions, showed less variability between samples than ^{241}Pu and ^{242}Pu (Table 1). Some of the variability of ^{241}Pu may be attributed to its short half life, 14.35 y, relative to the other isotopes: ^{239}Pu ($t_{½}$ = 24,100 y), ^{240}Pu ($t_{½}$ = 6,560 y), and ^{242}Pu ($t_{½}$ = 375,000 y).

The atomic mass ratios of $^{242}Pu/^{239}Pu$ versus $^{240}Pu/^{239}Pu$ are presented in Figure 2. The $^{240}Pu/^{239}Pu$ ratio for the weapons-grade Pu control was 0.0634 ± 0.0008. This value is consistent with Oughton et al. (2000) who reported that weapons-grade Pu generally has a $^{240}Pu/^{239}Pu$ atomic ratio of <0.07 (2000). $^{240}Pu/^{239}Pu$ values for both fallout control samples (0.183 ± 0.002 for the Anderson, South Carolina sample and 0.162 ± 0.004 for the Savannah River Site perimeter sample) agreed well with values reported by Kelley et al. (1999) for a soil sample collected in Raleigh, NC; they reported a $^{240}Pu/^{239}Pu$ ratio of 0.1811 ± 0.0009. They also agree with the global fallout average of 0.18 for atmospheric aerosol, soil, and ice core samples (Krey et al., 1976). The large $^{240}Pu/^{239}Pu$ difference between the weapons-grade and fallout control samples permits using this atomic ratio to distinguish between these two potential Pu sources. The four lysimeter sediments had very similar $^{240}Pu/^{239}Pu$ atomic ratios, ranging from 0.0630 ± 0.000040 to 0.06354 ± 0.000144. This range included the weapons-grade Pu control sample (0.06343 ± 0.000823), but not the two fallout control samples. Therefore, this isotopic ratio data indicates that the Pu in the lysimeter surface sediment originated from weapons-grade Pu, the source material used in the lysimeters.

$^{242}Pu/^{239}Pu$ ratios also provided strong signature differences between the fallout and the weapons-grade Pu used in the lysimeters. $^{242}Pu/^{239}Pu$ atomic ratios for the fallout control samples were near identical, about 0.0465, whereas the spike Pu control sample was 0.00051 ± 2.5E-5, a two order of magnitude difference. Again, this large difference between the two control samples permits using the $^{242}Pu/^{239}Pu$ atomic ratios to distinguish between these two potential Pu sources. The $^{242}Pu/^{239}Pu$ ratios for the four lysimeter samples ranged between 0.000375 to 0.000392, values strongly indicating the presence of the weapons-grade Pu.

3.2. Numerical Modeling

Typical simulations with plant Pu uptake (Simulations 2, 3, and 4) and without plant Pu uptake (Simulation 1) are shown in Figure 3a. Simulations 2, 3, and 4 differ with regards to the partitioning coefficient, K_{d_root} values (Pu concentration ratio of xylem to liquid (sap)), used to calculate Pu retardation in the xylem. As the retardation increases with increasing K_{d_root} partitioning between the xylem solution and xylem material, the amount of Pu retained in the root section increases while the amount being transferred into the shoots/leaves decreases (Figure 3b). The model captured the general behavior of the data in the top 20 cm of the lysimeter with the addition of the plant Pu uptake mechanism, except for the scattering which was attributed to the time-dependent and three dimensional growing of the roots by Demirkanli et al. (2009). One of the most important outcomes of these simulations was that the addition of root Pu uptake and xylem transport did not affect the model fit to the below-source portion of the data.

As mentioned earlier, Pu leaving from the upper boundary of the root model (top of the lysimeter) was assumed to go into the shoots. As can be seen in Figure 3b, the model predicts that some part of the total activity taken up by the roots is always transferred into the shoots, with the amount being dependent on the retardation in the root xylem. Thus, an accumulation of activity in the surface sediments is expected due to senescence of the Pu containing shoots as seen in the data. Even though the model takes annual decaying of the roots into account and transfers yearly the activity in the roots back into the lysimeter sediment, the activity accumulation in the surface sediment was incorporated into the model only for one simulation, shown in Figure 4, to demonstrate a possible effect of such a mechanism. The simulation in Figure 4 was the same as simulation 3 in Figure 3a with the addition of the transfer of activity in the shoots back into the top sediment yearly, representing the senescence of the leaves. As

expected, a mechanism describing leaf senescence may explain the increased concentrations in the lysimeter surface sediment.

4. Summary

This study is part of a long term lysimeter program design to provide insight into the fate and transport of Pu in the vadose zone. An unexpected result from this program was that a large proportion of the buried Pu source material had migrated upward. A hypothesis evolved that the surface accumulation of Pu was the result of Pu being taken up by plant roots, translocated to the above-ground portion of the plants, and then deposited as plant detritus on the ground surface (Demirkanli et al., 2009). This hypothesis stemmed from three observations: 1) elevated total Pu concentrations in some surface sediment samples collected at the lysimeter, 2) the intermittent presence of grasses growing on the lysimeters, and 3) modeling results (Demirkanli et al., 2009) suggesting that a substantial amount of Pu could be taken up by lysimeter plants during the 11 year experiment.

The objective of this study was to determine whether the surface sediment Pu originated from the buried source Pu (weapons-grade Pu) or from atmospheric deposition. This study demonstrated that with out question, the surface Pu had the isotopic signatures of the buried source. This provided additional confirmation that Pu had moved upward. Importantly, this is not direct evidence in support of plant uptake mechanism because that requires plant Pu data for several years. An alternative Pu transport mechanism is that the Pu moved upward as a result of animal activities, such as earth worms or ants. We have chosen to discount this latter mechanism because: 1) the sediment Pu concentration trend data in Figure 1 is too smooth for such bioperturbation transport, 2) the trend lines above the source terms, where animal populations are

361 greatest, are not more perturbed than those below the source terms, and 3) there was not any
362 evidence of animal galleys in the sediment cores. Consequently, in the lack of direct evidence
363 we have collected a preponderance of indirect evidence including computer simulations that have
364 ruled out such factors as evapotraspiration, enhanced Pu oxidation in the vadose zone, enhanced
365 water flow due to hysteresis (Demirkanli et al. 2009); and, new in this manuscript (Figure 3a),
366 we have reasonably simulated the upward sediment Pu concentration experimental data only
367 when we include plant uptake mechanism in our models. Finally, we have also reasonably
368 simulated the accumulation of Pu on surface sediments (Figure 4) by incorporating plant uptake.
369 To our knowledge, this is the first field observation, albeit indirect, of plants facilitating the
370 upward movement of Pu, or any other actinide. In the past, plants were not deemed important
371 transport vectors of actinides because it was repeatedly shown that plants took up very low Pu
372 concentrations with respect to sediment Pu concentrations. Simulations indicate that because
373 plants create a large water flux, small concentrations taken up in the plants over long durations
374 may result in a measurable accumulation of Pu on the ground surface. These results may have
375 implications on the pathway assumed for calculating risk associated with long-term stewardship
376 and monitored natural attenuation management of Pu contaminated subsurface and surface
377 sediments.
378

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380

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468 **List of Figures**

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487 of activity in the shoots back into the top sediment yearly. S/S_o is the Pu concentration (S) in the
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489 partitioning coefficient in the xylem between the xylem solution and xylem wall material.
490 Symbols represented measured values.

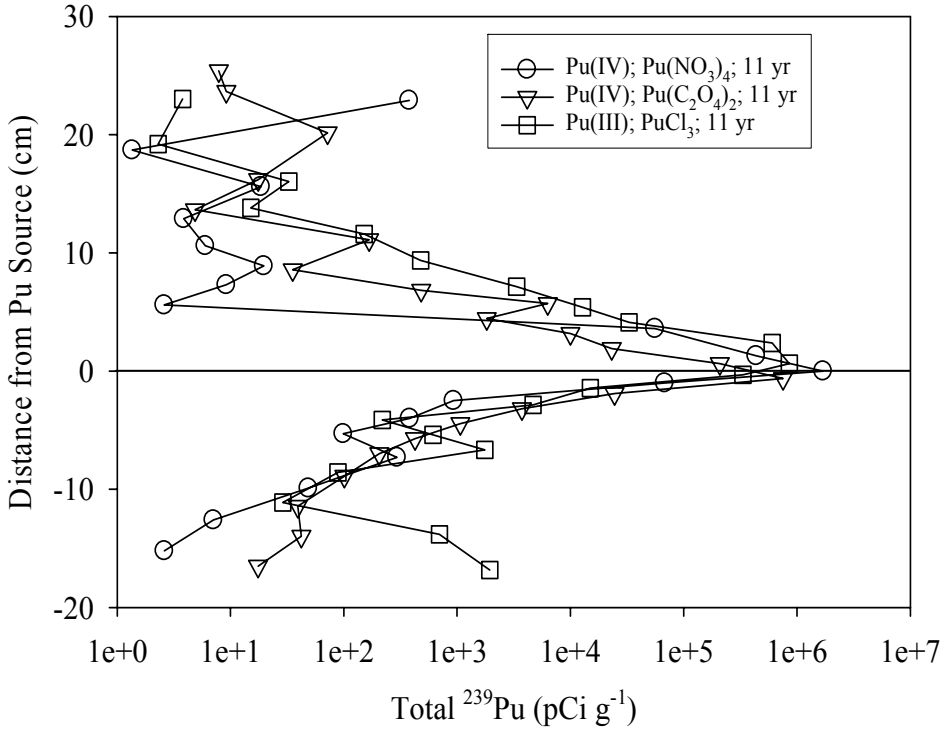


Fig. 1. Total Pu sediment concentrations in three lysimeters left exposed to natural weather conditions for 11 years.

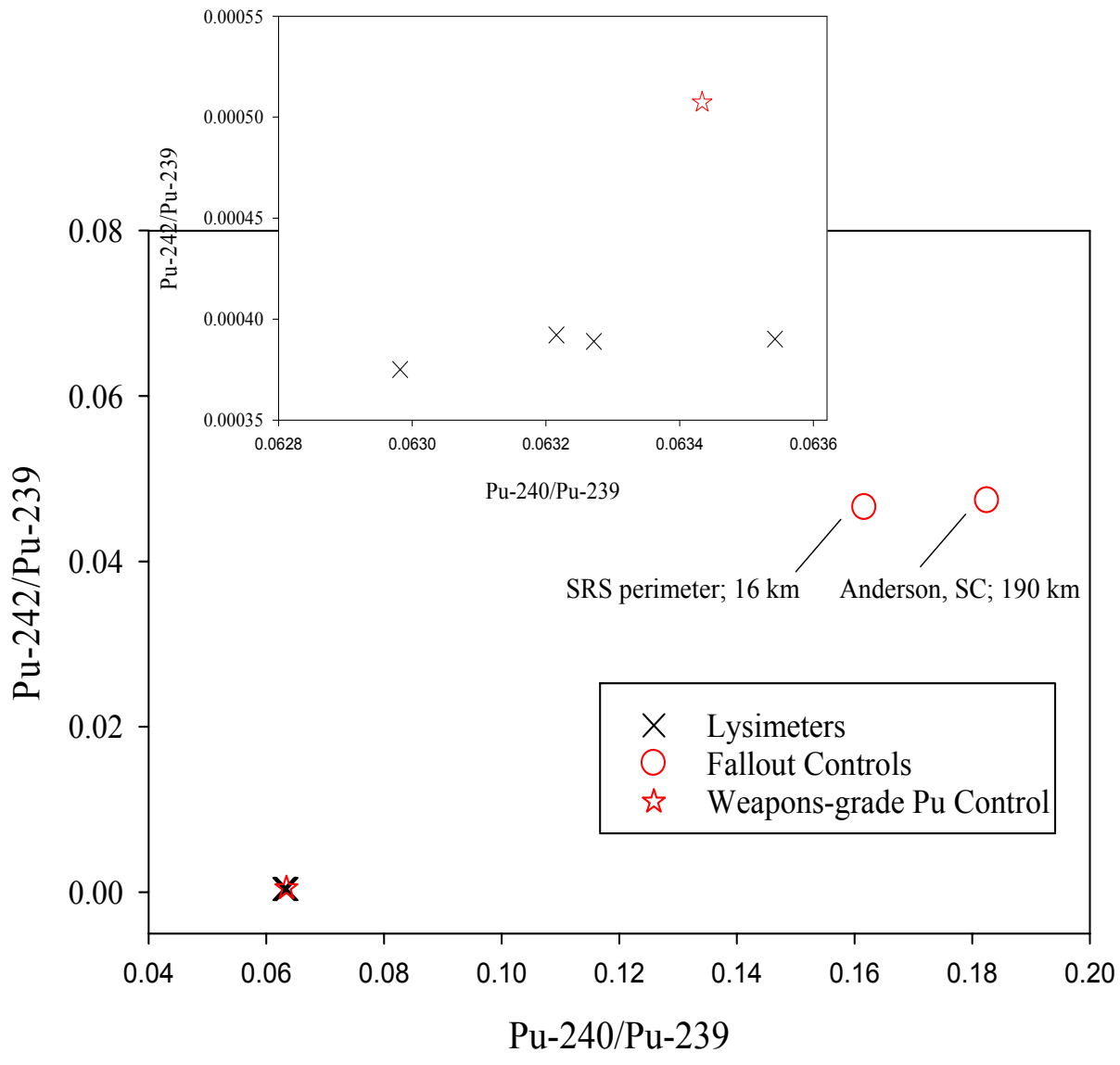
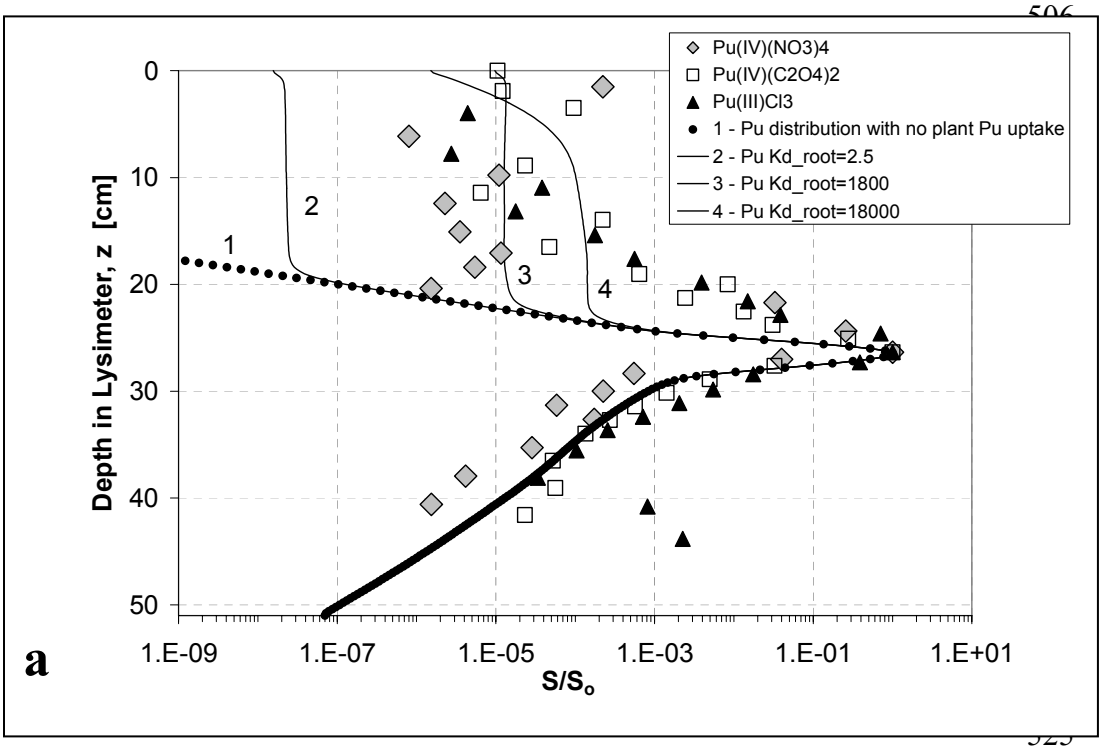


Fig. 2. Atomic ratios of $^{242}Pu/^{239}Pu$ versus $^{240}Pu/^{239}Pu$ for the four lysimeter surface sediment samples, two fallout control samples collected 16 and 190 km from the study site, and a positive control for the weapons-grade Pu used as spike material in the lysimeters. The larger graph demonstrates that the Pu isotopic ratios of the surface lysimeter sediments differ greatly from fallout control samples. Inserted graph demonstrates that the lysimeter surface sediments had similar isotopic ratios as a weapons-grade Pu control sediment.



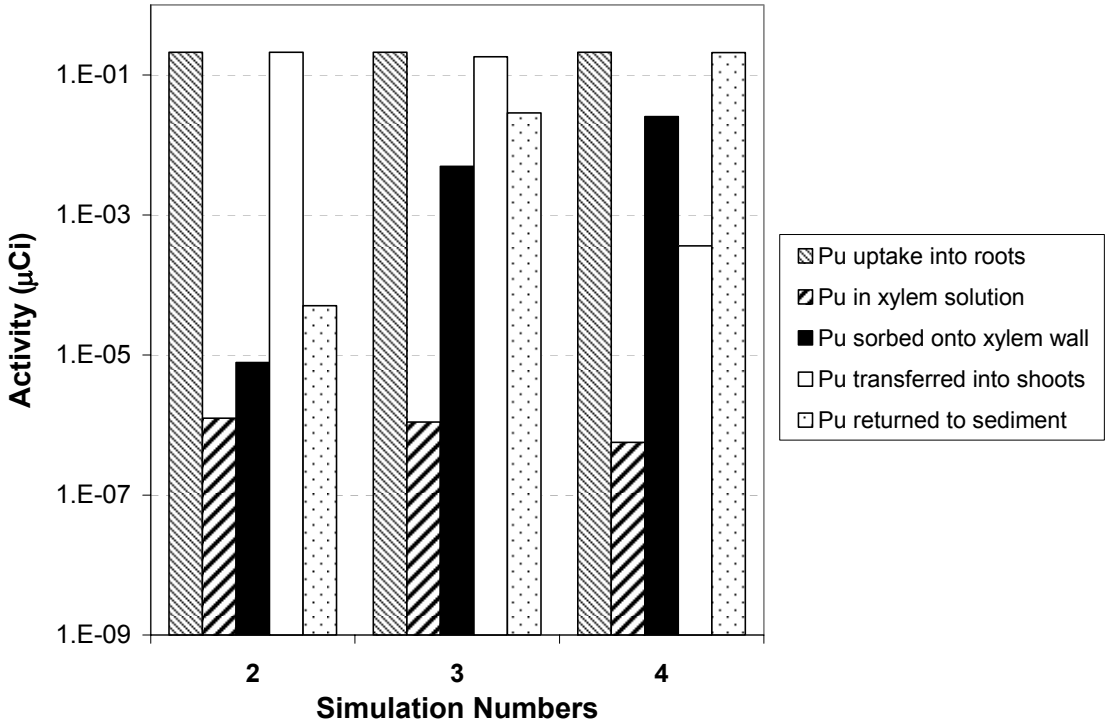


FIG. 3. (a) Simulations with and without Pu root uptake and xylem transport and varying Pu-root distribution coefficient values (K_{d_root}). (b) Activity distribution within different parts of the plant compared to the amount taken up into the plant and returned into the lysimeter sediment due to the yearly root decay. S/S_o is the activity concentration (S) in the sediment/root system divided by the activity concentration at the source location (S_o). K_{d_root} is the partitioning coefficient in the xylem between the xylem solution and xylem wall material.

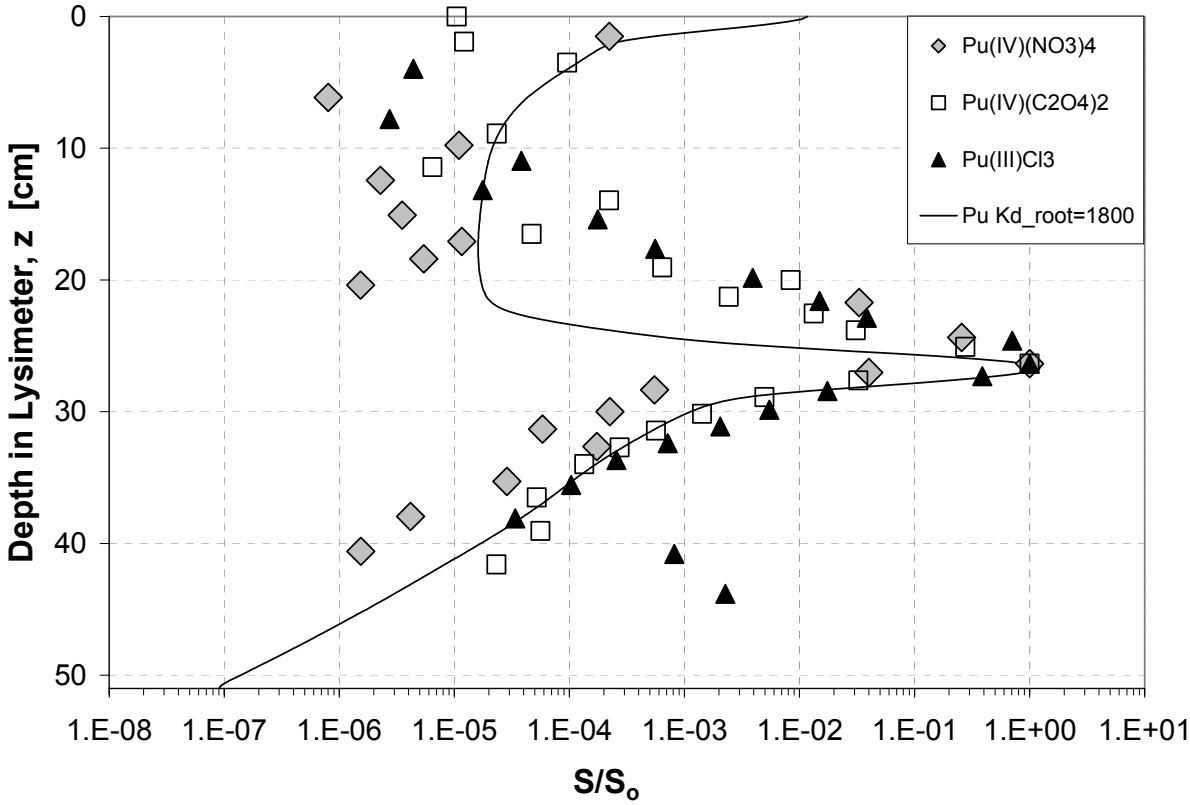


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Table 1. Pu isotope activity and atomic mass fractions in samples and controls.

Sample	^{238}Pu conc.	^{239,240}Pu conc.	^{239}Pu		^{240}Pu		^{241}Pu	
	(Bq g^{-1})	(Bq g^{-1})	fraction	2 sigma	fraction	2 sigma	fraction	2 sigm
$Pu(C_2O_4)_2$ Lysimeter	<0.10	0.30	0.9386	0.0006	0.059331	6.2488E-05	0.001763	5.99E-
$Pu(NO_3)_4$ Lysimeter	0.25	13.98	0.9388	0.0003	0.059125	3.2043E-05	0.001762	3.08E-
$PuCl_3$ Lysimeter	0.08	0.13	0.9385	0.0007	0.059379	7.1694E-05	0.001779	6.90E-
$Pu(OH)_4$ Lysimeter	<0.10	0.15	0.9382	0.0011	0.059617	1.1617E-04	0.001794	1.12E-
WG-Pu Source Control[(a)]	0.25	14.15	0.9382	0.0006	0.059658	6.5478E-05	0.001791	6.30E-
Fallout Control-16 km[(b)]	2.59E-5	3.737E-4	0.8596	0.0112	0.1390	2.6E-3	0.0015	0.00
Fallout Control-180 km[(b)]	<1.11e-5	4.551E-4	0.8446	0.0041	0.1542	1.1E-3	0.0012	0.00

[(a)] WG-Pu Source Control = Weapons-grade Pu source material
[(b)] Fallout Controls were collected from the perimeter of the SRS, Aiken, SC USA located 16 km from the lysimeter site and from Ande
km from the lysimeter site, respectively.
[(c)] ^{242}Pu concentrations are not available for these samples because this isotope was added to provide percent Pu recovery data. This yi
mass spectrometer to provide Pu concentration data. The "0.04 value" was taken from Kelley et al. (1999), for a sample collected in R

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