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## Enhanced Plutonium Mobility During Long-Term Transport Through an Unsaturated Subsurface Environment

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### ABSTRACT

Plutonium moved more rapidly through vadose zone sediments than previous thought possible. Based on field studies conducted for up to 11 years and supplemental laboratory studies, it was hypothesized that periodic sediment drying caused the very slow release of tightly bound Pu into the mobile aqueous phase, presumably by oxidation of Pu(IV) to the more mobile Pu(V). Of particular interest, was that this release occurred in sediments, that when saturated with groundwater, promoted rapid reduction of Pu to the less mobile form, Pu(IV). Accurate prediction of Pu transport through the vadose zone is important because this region is expected to provide an important buffer between disposed nuclear waste and the biosphere.

### TEXT

A large stockpile of nuclear waste generated from the fabrication of defense materials and spent nuclear fuel is, and will be, disposed of in engineered facilities located in the vadose zone, the unsaturated region between the surface soil and the underlying aquifer. The amount of material placed in these facilities is based on risk calculations, which account for the rate various radionuclides migrate through geologic material towards a hypothetical receptor.

Plutonium is a key risk driver amongst the long-lived nuclear waste material being considered for burial. Plutonium solubility and mobility in geologic environments is largely controlled by its oxidation state. In reduced states of +3 or +4, it is several orders of magnitude less soluble and less mobile than in oxidized states, +5 and +6 (1). The pH and Eh of natural environments is such that Pu often exists simultaneously as Pu<sup>4+</sup> and Pu<sup>V</sup>O<sub>2</sub><sup>+</sup>, and to a far smaller extent as Pu<sup>3+</sup> and Pu<sup>VI</sup>O<sub>2</sub><sup>2+</sup> (2 – 4). Some Fe(II)-bearing minerals (3, 5), organic matter (5), and natural sediments (6) can reduce Pu from the mobile oxidized forms to the less mobile reduced forms. These findings have prompted the implicate assumption in most risk calculations involving existing and proposed repositories that once Pu is breached from the waste form, Pu<sup>IV</sup>O<sub>2</sub>(s), into the surrounding geologic material, it will remain in a reduced form.

This study was conducted at the Savannah River Site (SRS), Aiken, South Carolina and reports the movement of Pu through sediment lysimeters exposed to natural precipitation over a 2- to 11-yr period. Approximately 1.7 x 10<sup>7</sup> Bq (3.4 x 10<sup>-5</sup> moles) of aqueous weapons grade Pu was added as Pu<sup>VI</sup>O<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> or Pu<sup>IV</sup>(NO<sub>3</sub>)<sub>4</sub> to filter papers, that were buried 21.6 cm below the sediment surface. The lysimeters consisted of inverted 50-L carboys with their bottoms cut off and were connected to separate leachate collection reservoirs that were periodically sampled for

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total aqueous Pu concentrations (Figure 1). At the end of the study, total Pu concentrations were measured in 1.25- or 2.5-cm, depth-discrete, sediment samples.

After 2 years of exposure to 245 cm precipitation, the Pu in the Pu(VI) lysimeter had migrated in a somewhat log-normal manner below the source (Figure 2). Pu concentrations above background were detectable as deep as 25-cm. Essentially no Pu was detected in the leachate samples, with only a few scattered samples containing Pu concentration above background levels.

Plutonium migrated appreciably less in the Pu(IV)-amended lysimeter than in the Pu(VI)-amended lysimeter, even though it had been left in the field 9 years longer and had received 1045 cm more precipitation (Figure 3). Plutonium concentrations decreased on average an order-of-magnitude per centimeter for the first 5 cm below the source, an astounding rate of contaminant retardation. Plutonium was detectable at concentrations above background at a depth of 12 cm beneath the source. As was the case with the leachate from the Pu(VI)-amended lysimeter, essentially no Pu was detected in the leachate samples.

In an attempt to understand the important geochemical mechanisms responsible for these two sets of Pu depth profile data, supplemental laboratory studies and reactive transport modeling were conducted. In the first laboratory study, Pu(V) was added to a series of tubes containing similar sediments as used to fill the lysimeters and then the oxidation state of Pu on the sediment was determined (Figure 4) (7). Plutonium(VI) was not used in these studies because earlier studies indicated that it was extremely unstable at typical groundwater pH values and quickly reduced to Pu(IV) and Pu(V), consistent with thermodynamic calculations (**Error! Reference source not found.**). The concentration of Pu(V) decreased over time, coinciding with an increase in Pu(IV). A first-order reduction rate constant of  $0.118 \pm 0.007 \text{ hr}^{-1}$  was calculated from the disappearance of Pu(V) from the system. This reduction is thought to be induced by various Fe(II)-bearing minerals commonly identified in these sediments, such as ilmenite ( $\text{FeTiO}_3$ ), biotite ( $\text{K[Mg,Fe]}_3[\text{Al,Fe}]\text{Si}_3\text{O}_{10}[\text{OH,F}]_2$ ), and magnetite/magnemite ( $\text{Fe}^{+2}\text{Fe}_2^{+3}\text{O}_4/\text{Fe}_2\text{O}_3$ ) (8).

Another experiment was conducted to determine whether sorbed Pu from the Pu(IV) lysimeter could be desorbed into the aqueous phase under natural oxidative conditions. The sediment sample with the highest Pu concentration from the Pu(IV) lysimeter, the sample that originally held the Pu(IV) source, was agitated in a groundwater slurry under an Ar(g) (reducing) environment for 14 days to promote Pu(IV) formation as a starting point for the experiment. A portion of this sediment was then exposed to 80 days of biweekly cycling through wet and dry conditions (10), while a second portion of this sediment was left in the Ar environment. The aqueous phase of the wet/dry and Ar treatments were periodically sampled for total Pu concentrations. Plutonium aqueous concentrations in the reduced system remained below detection limit ( $<25 \text{ Bq L}^{-1}$ ) throughout the sampling period (Figure 5). Conversely, aqueous Pu concentrations in the wet/dry-cycled samples increased during the 80 day trial. First-order kinetics with respect to the solid phase Pu concentrations, were modeled for the generalized equation:  $\text{Pu}(s) + \text{O}_2 \rightarrow \text{Pu}(aq)$ , producing a pseudo first-order rate constant of  $1.4 \times 10^{-6} \text{ hr}^{-1}$  (11). This value is 4 to 5 orders-of-magnitude slower than the reduction rates measured in SRS sediments (12) and pure Fe mineral phases (5). Assuming Pu oxidation is responsible for the release of Pu from the sediment, the governing equation responsible for the release of Pu from the sediment can be rewritten as:  $\text{Pu}^{+4}(s) + \text{O}_2(aq) + \text{H}_2\text{O} \rightarrow \text{PuO}_2^+(aq) + \text{H}_2\text{O}$ .

The sediment Pu concentration profiles in Figure 2 and Figure 3 were modeled using a geochemical transport code (13) that numerically described the key Pu geochemical reactions

observed in these and previous experiments (12). The model assumed all Pu existed in the +4 and +5 oxidation states, the dominant species measured in simulated SRS groundwater (14). In the case of the Pu(VI)-amended lysimeter, the Pu was assumed to rapidly convert to Pu(V) (7). The model included (1) equilibrium partitioning of Pu(IV) and Pu(V) between the aqueous and sorbed phase as defined by pH-dependent, oxidation-state specific distribution coefficients, (2) kinetic reduction and oxidation between Pu(IV) and Pu(V) in the sorbed phase, and (3) steady-state saturated transport.

When only sorption and no oxidation/reduction was assumed to occur in the Pu(VI)-amended lysimeter, the simulation greatly overestimated Pu migration (Simulation 1 in Figure 2). Furthermore, the simulated curve did not capture the shape of the measured results, indicating that the discrepancy was not the result of an inaccurate sorption value (a value based on the data in Figure 4). If the Pu(V/VI) was assumed to rapidly convert to Pu(IV), then the simulation greatly underestimated Pu migration (Simulation 2 in Figure 2). Again, this simulation did not capture the shape of the measured results. A better fit to the data was obtained by using a more moderate reduction rate of  $2 \times 10^{-4} \text{ hr}^{-1}$ , consistent with previously measured values (5, 12) (Simulation 3, Figure 2). These simulations support the contention that surface enhance reduction of Pu(V/VI) is important and that over the 2-yr duration of this trial, reoxidation of Pu(IV) had limited impact on Pu mobility (Simulation 3 vs. Simulation 4).

For the Pu(IV) amended system, the model greatly underestimated Pu mobility when Pu(IV) was assumed to equilibrate between the aqueous and sediment without any oxidation occurring (Simulation 1 in Figure 3). Conversely, when Pu(IV) was permitted to oxidize very rapidly ( $1 \times 10^{-5} \text{ hr}^{-1}$ ), the model greatly overestimated actual Pu mobility (Simulation 2 in Figure 3). Using the oxidation rate calculated from the data in Figure 5,  $1.4 \times 10^{-6} \text{ hr}^{-1}$ , a reasonable fit was obtained to the magnitude, and more importantly, to the shape of the data (Simulation 3 in Figure 3).

A deficiency of this study is that it does not provide direct spectroscopic oxidation state information about the Pu on the sediment or in the aqueous phase. Sediment Pu concentrations were generally too low for such analytical techniques as x-ray absorption spectroscopy (XAS) and x-ray photoelectron spectroscopy (XPS) techniques to provide useful information (15). Short of having this type of conformational data, we have developed a working hypothesis to describe the mechanisms controlling Pu transport in this unsaturated system. During transport through the vadose zone, Pu is cycled through the +4 and +5 oxidation states as the redox status of the system changed in response to wetting and drying cycles. In the +4 oxidation state, Pu was largely immobile, with a retardation factor (ratio of the velocity of water divided by the velocity of Pu) more than 2 orders-of-magnitude greater than that for Pu(V). The periodic introduction of oxygenated water by direct rainfall or the diffusion of pore space  $\text{O}_2(\text{g})$  into the groundwater, promoted the slow oxidation of Pu to the +5 state. Pu(IV) oxidation may also have resulted from the surface enhanced reaction with  $\text{MnO}_2$  (discussed below). In the +5 state, the Pu was much more mobile, but was quickly reduced to the +4 state by surface-enhanced reduction reaction.

Several recent studies have shown that Pu(IV) can be oxidized to Pu(V/VI) by Mn-oxides phases (16 – 19). These minerals have not been detected on SRS sediments, but presumably exist as redoximorphic features in aquatic sediments, such as nodules and concretions formed as a result of redox changes. Such features clearly were not evident in the lysimeter sediments; not surprisingly since the sediment is bright red, an indication of a well aerated/oxygenated system. Furthermore, the Mn concentrations in these sediments were moderately low,  $630 \text{ mg kg}^{-1}$ , and

existed primarily as adsorbed species and sediment coatings comprised of Fe/Al/Mn-oxyhydroxide solid solutions. Although surface enhanced oxidation by Mn can not be totally ruled out, it is our opinion that its role, if any, is appreciably less than that of O<sub>2</sub> diffusion.

Mobile colloids have also been shown to enhance Pu mobility (20 – 22). It is possible that a very small fraction of the mobile Pu moved with colloids, but this small fraction would not be detectable by the non-concentrating leachate sampling techniques used in this study. As mentioned above, essentially no Pu was detected in the leachate samples, either in the aqueous or colloidal form. Furthermore, mobile colloids could not be responsible for the Pu depth profile data; colloid-facilitated transport would manifest itself as a second Pu concentration peak in this type of data.

It is important to note that these simulations did not explicitly model the changing moisture conditions in the sediment during the 2 or 11 years scenarios, the data needed to conduct such modeling are not available. Instead, it assumed a steady state saturated flow conditions, a hydrological assumption that contradicts the proposed chemical model of how O<sub>2</sub>(g) may diffuse in the aqueous/solid system. This simplification was introduced because data are not available to fully parameterize a non-steady state, unsaturated flow transport model and to maintain parsimony.

The transitory transport involving the proposed cycling of Pu +4 and +5 has not been previously reported because of a number of unique attributes of this data set. First, its long duration permitted this slow phenomenon to manifest itself in a measurable manner. Even the study conducted for 2 yr (Figure 2), was not sufficiently long to discern differences between simulations run with oxidation (Simulation 4) and without oxidation (Simulation 3) of Pu(IV). Previous laboratory Pu transport studies have been conducted over time periods of days to weeks (12, 17), certainly not long enough to discern a reaction with a rate in the order of 10<sup>-7</sup> hr<sup>-1</sup>. Secondly, oxidation state of the starting material was well characterized as compared to previous long-term field studies where the Pu was placed with other waste materials and in unknown oxidation states (20 – 22). Finally, essentially all Pu (geo)chemistry studies involving oxidation state have been conducted under constant saturated condition (3, 5). Such studies provide needed controls to permit mechanistic understanding of Pu geochemistry, but are not designed to provide insight into transitory processes, such as fluctuating water saturation or redox status.

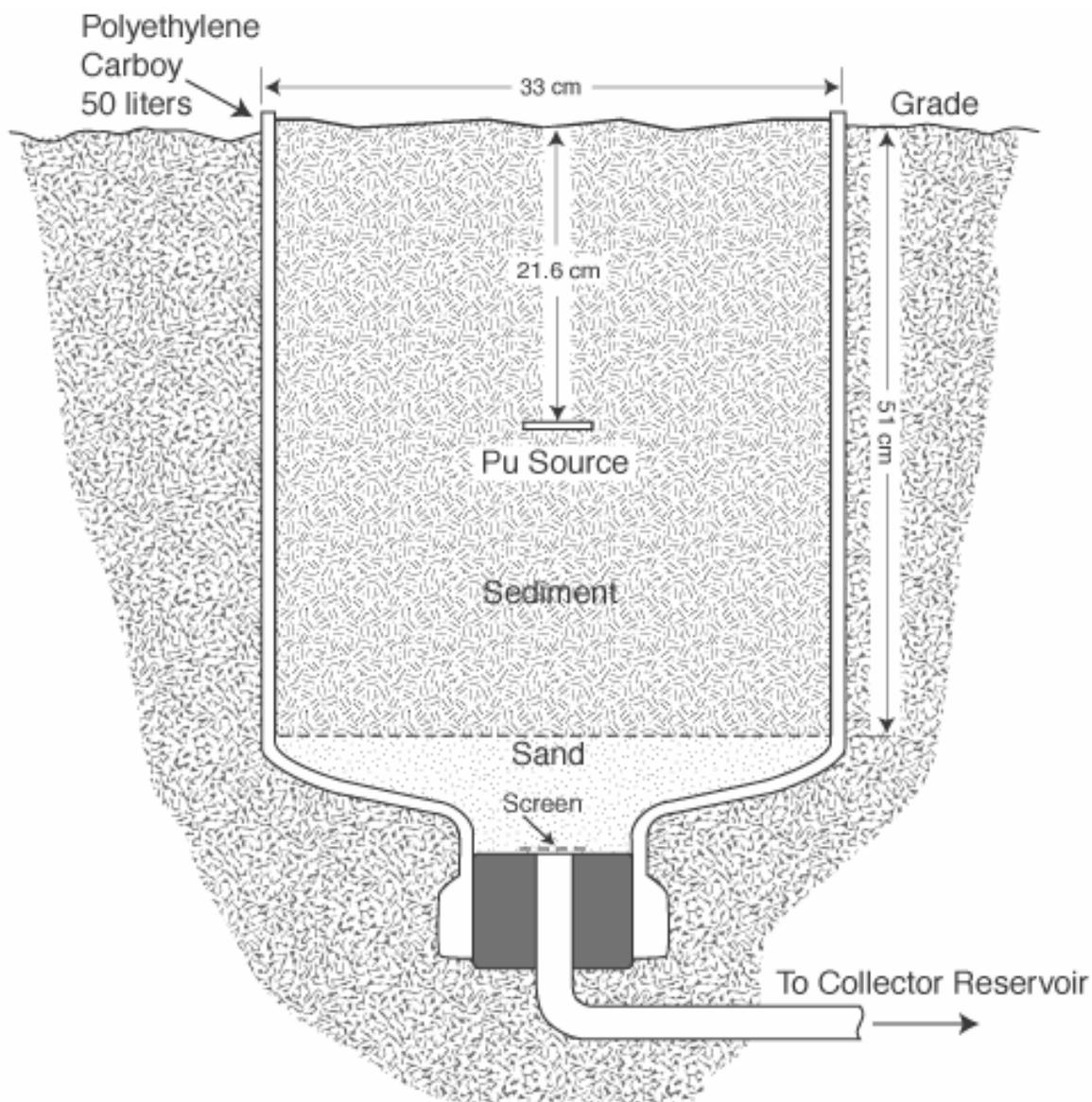
This study showed that Pu(V) reduction can occur not only in pure mineral isolates, but also in naturally occurring sediments. It also showed that natural oxidation processes, approximated by biweekly wet/dry cycles, can promote Pu desorption, presumably by oxidation of Pu(IV). Especially important is that the Pu oxidation was induced in a sediment that under saturated conditions promoted Pu(V) reduction. Transport modeling supported the contention that Pu oxidation occurred in the lysimeter system; the inclusion of an oxidation term in simulations produced curves that captured the shape of the sediment Pu concentration data. The vadose zone is expected to provide an important buffer between disposed nuclear waste and the biosphere. For example, the vadose zones at the SRS and Hanford Site are expected to account for >95% of the Pu residence time as it travels between disposal sites and hypothetical receptors (23, 24). Transport models that take into account only sorption and solubility may therefore underestimate the extent Pu migrates through the subsurface.

## References and Notes

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7. A  $^{239}\text{Pu(V)}$  spike was added to  $24,300 \pm 400 \text{ mg L}^{-1}$  suspensions of SRS control lysimeter soil in  $0.02 \text{ M NaCl}$  to yield a final plutonium concentration of  $1.6 \times 10^{-8} \text{ M Pu(V)}$ . As a function of time, the oxidation state of the Pu on the sediment was determined by the method of Morgenstern and Choppin (A. Morgenstern, G. R. Choppin, *Radiochim. Acta.* **90**, 69 (2002)). This method involves desorbing Pu from the sediment and then applying ultrafiltration/ solvent extraction techniques to determine Pu oxidation states: thenoyl-trifluoroacetone (TTA) and di-(2-ethylhexyl)phosphoric (HDEHP). Results from control and oxidation state analog samples are presented as Supplemental Online Material.
8. Aqueous Pu(VI) was unstable in slightly acidic solutions, similar to SRS groundwater, without the presence of an oxidant or complexant. Low concentrations of Pu(VI) solutions prepared in  $1.0 \text{ M HNO}_3$  and  $10^{-3} \text{ M KMnO}_4$  had reduced to  $>90\%$  Pu(V) within two days following dilution in  $0.02 \text{ M NaCl}$  to pH 5.
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10. A 15-g aliquot of sediment was taken from an Ar (reducing) environment and placed on the top section of a disposable  $0.22\text{-}\mu\text{m}$  filtration assembly unit located on a laboratory bench top, an oxidizing environment. The sediment was cycled through two wet/dry cycles per week. During the wet cycle,  $\sim 1$  cm uncontaminated, air-sparged, SRS ground water ( $25\text{-mL}$ ) covered the sediment for 1 day. The water was then vacuum filtered through the sediment, and the sediment was permitted to air dry for 2 to 3 days, being completely air dried for at least one day. The air-dried sediment sample contained  $\sim 5.9\%$  moisture, as determined gravimetrically by drying at  $105^\circ\text{C}$ . pH and Eh was measured in the sediment slurry during the wet cycle and Pu concentrations were measured in the filtrate at the end of the wet cycle.
11. The first order with respect to solid phase Pu concentrations rate generated from the data in Figure 5 was corrected for adsorption assuming the appropriate  $K_d$  taken from Figure 4). This is not a well controlled experiment for quantifying kinetic terms because both moisture and  $\text{O}_2(\text{aq})$  concentrations varied in an uncontrolled manner through out the experiment. The good agreement between the pseudo-first order rate value generated from the wet/dry-cycling study and the reactive transport modeling were unexpected. One explanation for the good agreement between these two independent methods of estimating the Pu(IV) oxidation rate is that the laboratory technique captured most of the important chemical and hydrodynamic processes. Attempts to more rigorously control moisture and  $\text{O}_2(\text{aq})$  concentrations though studies in which air was sparged into a sediment slurry, resulted in a rapid decline in aqueous Pu concentrations as a function of time. We believe the introduced oxygen promoted a microbial bloom, which adsorbed Pu from the aqueous phase.

12. R. A. Fjeld, S. M. Serkiz, P. L. McGinnis, A. Elci, D. I. Kaplan, *J. Contam. Hydrol.* (in press) (2004).
13. Provide description of transport code and reference to more detailed information in Supporting Online Material.
14. Aqueous Pu oxidation state distribution in an SRS sediment and simulated groundwater system ~3 hours after spiked with Pu(V) was: at pH 3,  $1 \pm 1\%$  Pu(III),  $1 \pm 1\%$  Pu(IV),  $82 \pm 5\%$  Pu(V), and  $17 \pm 4\%$  Pu(VI); and at pH 5  $0 \pm 1\%$  Pu(III),  $1 \pm 1\%$  Pu(IV),  $93 \pm 2\%$  Pu(V), and  $5 \pm 1\%$  Pu(VI). Analyses were conducted by the thenoyltrifluoroacetone (TTA)/di(2-ethylhexyl)orthophosphoric acid (HDEHP) extraction techniques (M. P. Neu, D. C. Hoffman, K. E. Roberts, H. Nitsche, R. J. Silva, *Radiochim. Acta*, **66**, 265 (1994)). Insufficient aqueous Pu existed in systems spiked with Pu(IV) to measured Pu oxidation state distributions. Importantly, these reflect the aqueous phase and not the solid phase or total Pu oxidation state distribution.
15. To provide solid phase Pu oxidation state data at low Pu concentrations for interpreting this data, we are working on a selective sediment extraction technique (modification of method in Morgenstern and Choppin (19), coupled with an established selective aqueous phase extraction technique for Pu oxidation state analyses of the liquid extracts (M. P. Neu, D. C. Hoffman, K. E. Roberts, H. Nitsche, R. J. Silva, *Radiochim. Acta* **66**, 265 (1994)). Early results from this methods development have been presented: B. A. Powell, R. A. Fjeld, D. I. Kaplan, J. T. Coates, *Plutonium(VI) Reduction on Synthetic Hematite ( $\alpha$ - $Fe_2O_3$ ) and Magnetite ( $Fe_3O_4$ )*, American Chemical Society's 226<sup>th</sup> National Meeting, New York, NY, 7 – 11 September 2003.
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25. Work at Westinghouse Savannah River Company (WSRC) was performed under the auspices of the U.S. Department of Energy (DOE) contract DE-AC09-96SR18500. This project was supported by DOE's EMSP program, and WSRC's Mini-Sabbatical Program.



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Figure 1. Schematic of Savannah River Site lysimeters. Source consisted of Pu(IV) or Pu(VI) added as a liquid to filter paper and then sandwiched between two clean filter papers. Lysimeters were left exposed to natural precipitation for 2 or 11 years.

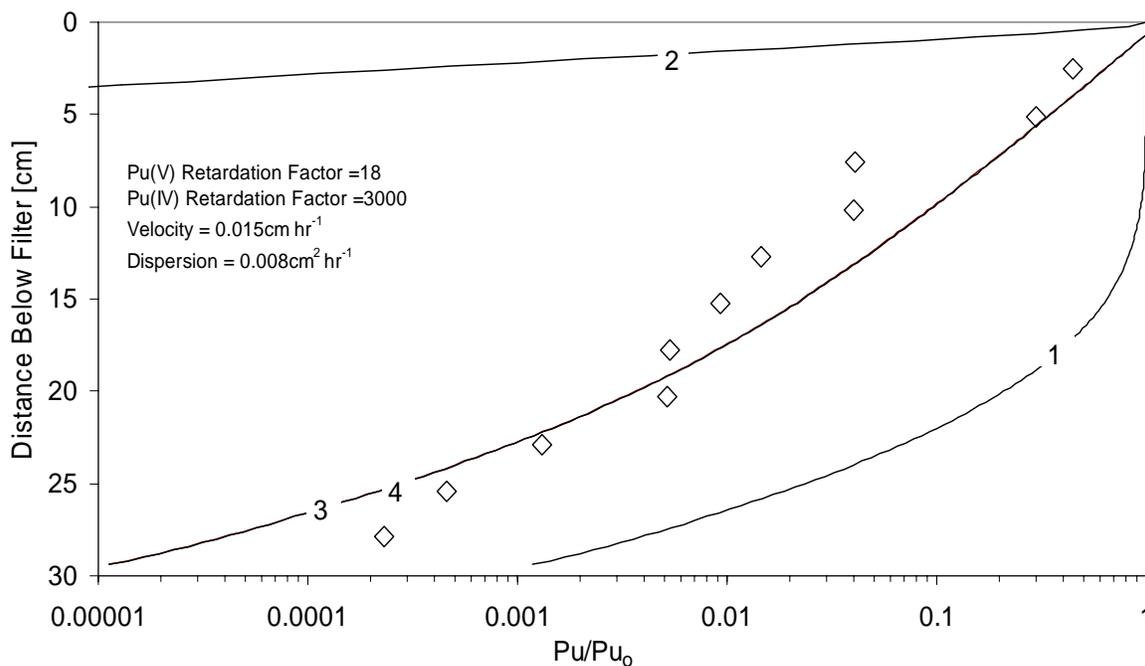


Figure 2. Normalized total Pu sediment concentrations ( $\text{Pu}/\text{Pu}_0$ ) in the  $\text{Pu}^{\text{VI}}\text{O}_2(\text{NO}_3)_2$ -amended lysimeter. Simulation input values ( $k_o$  and  $k_r$  are the first-order rate constants for Pu(IV) oxidation and Pu(V/VI) reduction, respectively): (1)  $k_o = 0 \text{ hr}^{-1}$ ,  $k_r = 0 \text{ hr}^{-1}$ ; (2)  $k_o = 1\text{e-}5 \text{ hr}^{-1}$ ,  $k_r = 0 \text{ hr}^{-1}$ ; (3)  $k_o = 0 \text{ hr}^{-1}$ ,  $k_r = 2.0\text{e-}4 \text{ hr}^{-1}$ ; and (4)  $k_o = 1.0\text{e-}6 \text{ hr}^{-1}$ ,  $k_r = 2.0\text{e-}4 \text{ hr}^{-1}$ .

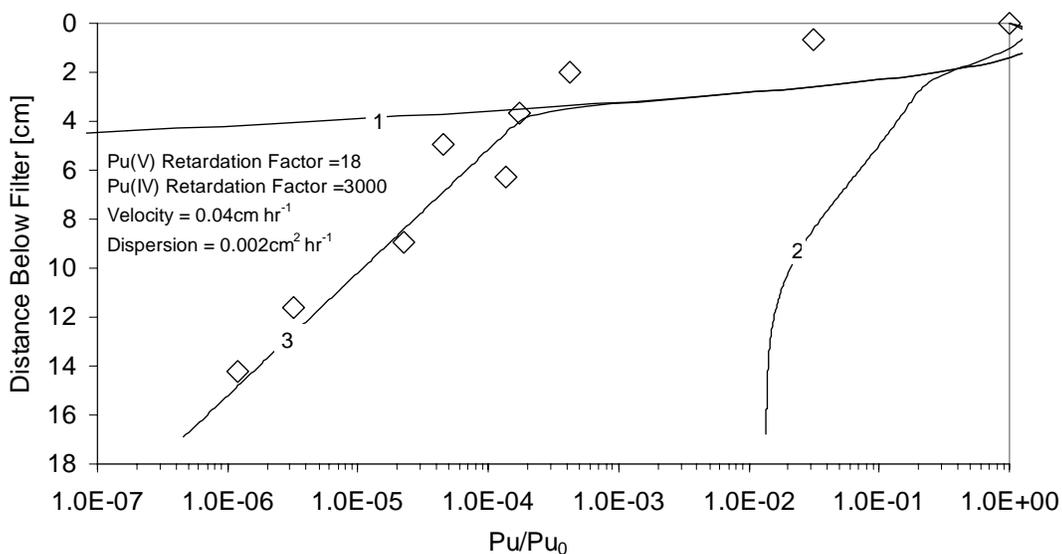


Figure 3. Normalized total Pu sediment concentrations ( $\text{Pu}/\text{Pu}_0$ ) in the  $\text{Pu}^{\text{IV}}(\text{NO}_3)_4$ -amended lysimeter. Simulation input values ( $k_o$  and  $k_r$  are the first-order rate constants for Pu(IV) oxidation and Pu(V/VI) reduction, respectively): (1)  $k_o = 0 \text{ hr}^{-1}$ ,  $k_r = 0 \text{ hr}^{-1}$ ; (2)  $k_o = 1\text{e-}5 \text{ hr}^{-1}$ ,  $k_r = 0 \text{ hr}^{-1}$ ; (7)  $k_o = 1\text{e-}8 \text{ hr}^{-1}$ ,  $k_r = 1.2\text{e-}3 \text{ hr}^{-1}$ .

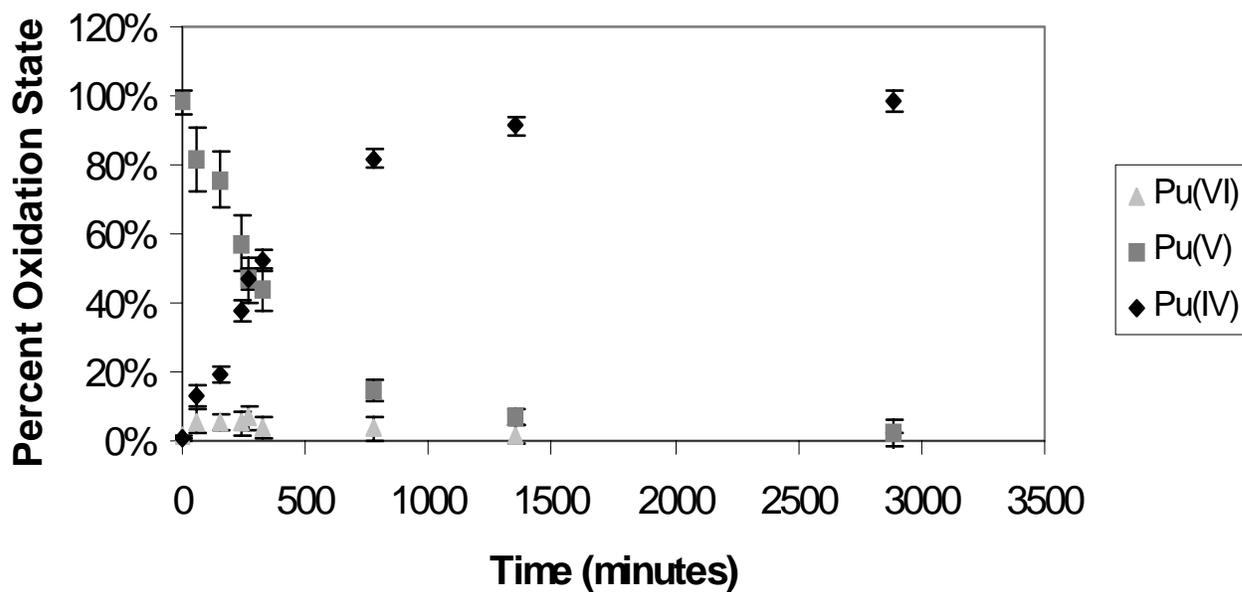


Figure 4. Oxidation state of sediment Pu following aqueous Pu(V) addition to an SRS Lysimeter Sediment suspension (suspended solids =  $25,000\text{mg L}^{-1}$ ; background electrolyte =  $0.02\text{M NaCl}$ ; mean and standard deviation of 2 replicates).

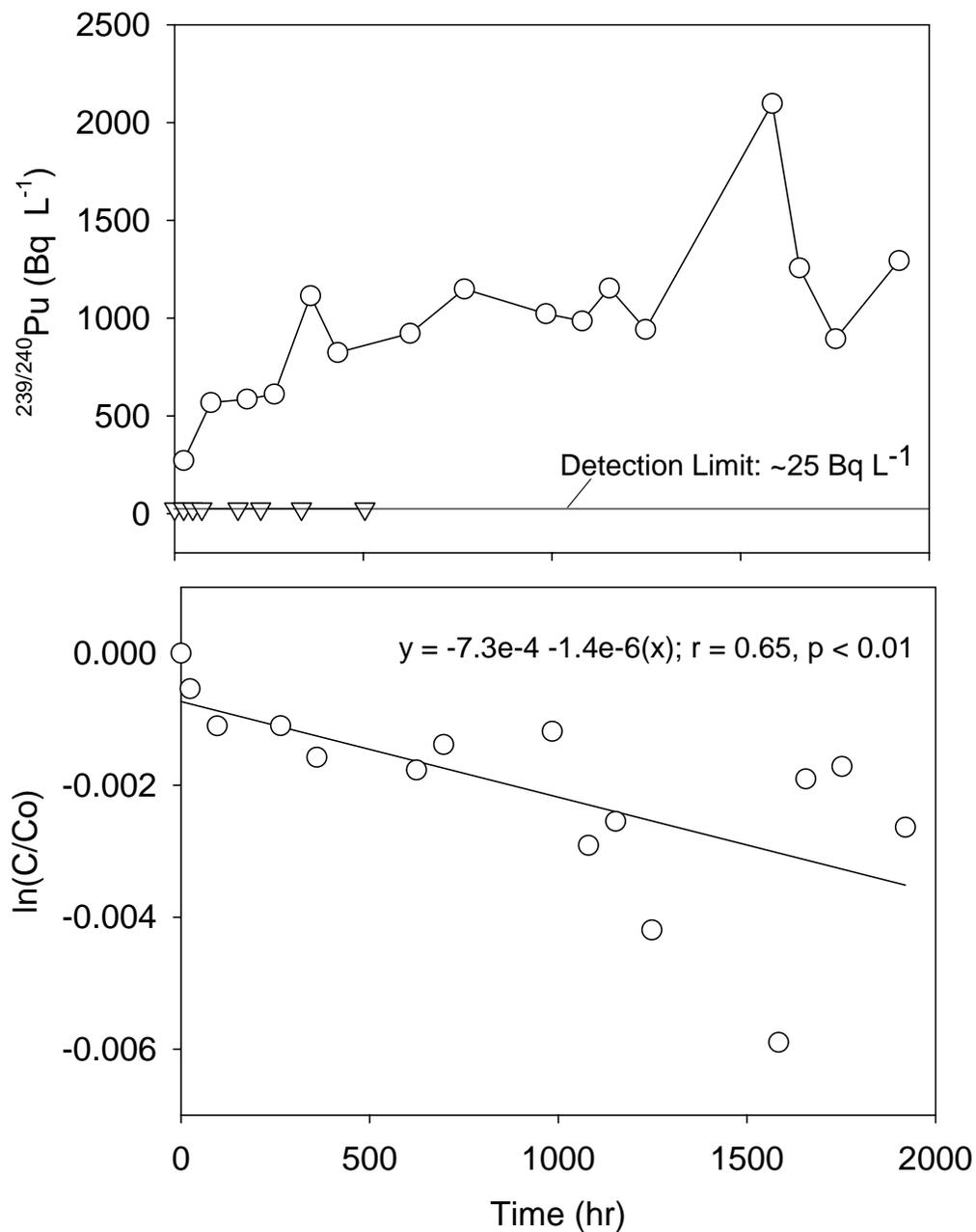


Figure 5. Top: Pu sediment desorption under oxidized (○) and reducing (▽) conditions from lysimeter containing  $\text{Pu}^{\text{IV}}(\text{NO}_3)_4$ . Under reducing conditions (Ar environment; Eh (SHE) =  $323 \pm 7\text{mV}$ ,  $\text{pH} = 7.2 \pm 0.2$ ), no Pu was detected in the aqueous phase. Under oxidizing conditions (sample placed through biweekly dry-wet cycling; Eh (SHE) generally cycled from 430 to 380 mV and pH from 6.2 to 6.5), aqueous Pu concentrations increased over time. Bottom: Pseudo-first order kinetics with respect to Pu on the solid phase; rate constant of  $1.4 \times 10^{-6} \text{ hr}^{-1}$ .