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Plutonium Transport Through Lysimeters Exposed to Natural Weather Conditions for Two to Twelve Years (U)

Daniel I. Kaplan[a], Deniz I. Demirkanli[b],
Robert A. Fjeld[b], Fred Molz[b], Brian Powell[b], Darrick Reid [b], Steve M. Serkiz[a]

[a] Westinghouse Savannah River Company
[b] Clemson University

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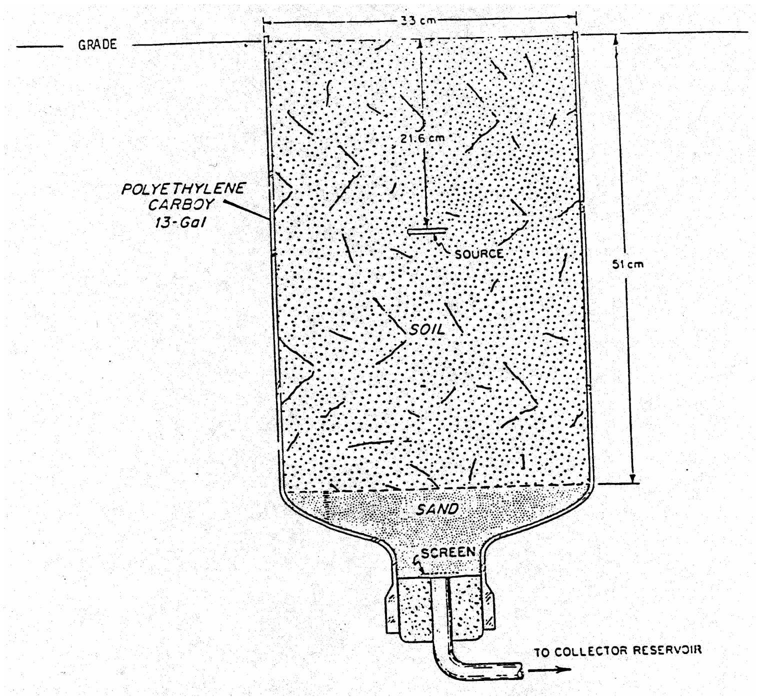

Westinghouse Savannah River Company
Savannah River Site
Aiken, SC 29808

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1.0 EXECUTIVE SUMMARY

One of the most important factors influencing the subsurface transport of plutonium (Pu) is its oxidation state. Under similar geochemical conditions (e.g., groundwater pH) the mobility of reduced Pu, Pu(IV), is two to three orders of magnitude lower than that of oxidized Pu, Pu(V) and Pu(VI). However, due to a poor understanding of Pu oxidation state transformations, transport models typically employ conservative assumptions which can lead to overly conservative and costly decisions. The objective of this study was to develop a conceptual geochemical transport model to describe Pu mobility through 52-L lysimeters established in 1980 (Mersman 1982, Hooker and Root 1981). The lysimeters contained E-Area sediment and various forms of well-characterized Pu sources of known oxidation state and were exposed to natural SRS weather conditions for up to ~11 years. For this study, archived core sediments from the lysimeters were retrieved and Pu concentrations in depth-discrete samples were measured and then transport of Pu was modeled using a coupled reactive transport model. The geochemical conceptual model and input values included in the transport code were based on laboratory experiments.

The single most important finding from this work was regardless of the Pu oxidation state added to SRS sediments, it quickly converted to the less mobile Pu(IV) form. This was observed in laboratory batch experiments in which the weaker sorbing (more mobile) oxidized form of Pu, Pu(V/VI), was added to SRS sediments and within 33 days had transformed into a form that sorbed to the sediment in an manner identical to the reduced Pu(IV). Further support of the contention that the more mobile form of Pu was quickly converted to a less mobile form was provided by the lysimeters data. After 2 years in the sediment, >90% of the Pu placed in the lysimeter as Pu(VI) moved <5 cm. This Pu distribution clearly could not be modeled by assuming that the Pu remained in its more mobile, oxidized form. Modeling simulations assuming no reduction indicated that essentially all the Pu should have leached from the sediment core, contrary to experimental results showing that barely detectable concentrations leaching from the lysimeter accounting for <0.1% of the Pu originally added. To resolve this discrepancy a kinetic reduction rate term (measured from SRS burial ground sediment) was included to the model, which captured well the salient features of the data.

Laboratory studies with sediments from a Pu(IV)-amended lysimeter indicated that under highly oxidizing conditions (repeated wet-dry cycling of sediments with oxygenated water), it was possible to cause Pu(IV) to desorb from the sediment, presumably as a result of oxidation to the more mobile Pu(V) form. The rate and magnitude of Pu oxidation never approached those of Pu reduction; the fractional release of Pu from the sediment in this lysimeter never exceeded 0.003%. However, this extremely slow release of Pu from the sediment was necessary to include in our modeling to explain the observed Pu sediment distribution in a Pu(IV)-containing lysimeter. This lysimeter was exposed to SRS weather conditions for 11.75 years and 99% of the Pu was detected within 5 cm of where it was placed. The transport of the remaining Pu, albeit a small fraction, could only be explained if a slow rate of Pu(IV) reoxidation was included in the model. As was the case with the Pu(VI) lysimeter, essentially no Pu was detected in the leachate of the Pu(IV) lysimeter.

In conclusion, it is expected that Pu will exist primarily in the SRS subsurface environment in the relatively less mobile Pu(IV) form, irrespective of the oxidation state that it first enters the ground. This is important in light of new findings by Haschke and others (2000) indicating that $Pu^{IV}O_2$ is not the thermodynamically stable form as had previously been understood. Rather, some of the $Pu^{IV}O_2$ surface is oxidized in the presence of water, forming as much as 27% Pu(VI). Our research indicates that should this oxidation reaction occur to SRS buried waste, that once the Pu(VI) comes in contact with SRS sediments, it would almost entirely convert to Pu(IV) within a month. The lysimeter results provide important long-term data that support the removal of important overly conservative approaches presently used to calculate risk and performance assessment associated with groundwater Pu. These findings do not contradict previous Pu modeling efforts, including the E-/Area Low-Level Waste Performance Assessment (McDowell-Boyer et al. 2000) or the Special Analysis on Pu disposal in SRS trenches (Cook 2002). Instead, the results from this work could be used in future calculations to improve accuracy and reduce uncertainty and conservatism.

2.0 INTRODUCTION

2.1 PLUTONIUM GEOCHEMISTRY

Plutonium in the natural environment can exist in four different oxidation states: Pu(III), Pu(IV), Pu(V), and Pu(VI). The most thermodynamically stable form in the environment is $Pu^{IV}(OH)_4(s)$. In the aqueous phase, the predominant form is Pu(V), although the other three may also be present to some extent (Orlandini et al. 1985; Bondietti 1982, Rai et al. 1980, Bryan et al. 1994; Mahamid et al. 1995; Choppin et al. 1997; Capdevila et al. 1992). Because sorption depends on the charge density of the atom or molecule being sorbed, it follows that the different oxidation states of Pu interact differently with the soil. Chemical reactions within the groundwater, such as oxidation, reduction, complexation, and hydrolysis can greatly influence interaction with surfaces and consequent mobility of this element (Cleveland et al. 1983).

The reduced forms of Pu expected in the natural systems are the Pu^{3+}, Pu(III), cations and hydroxide complexes of Pu^{4+}, Pu(IV), cations, and the oxidized forms are $Pu^{V}O_2^{+}$ and $Pu^{VI}O_2^{2+}$. In general, the reduced forms are predominant in acidic solutions, and the oxidized forms are predominant in basic solutions. However, in many systems several of these oxidation states may coexist in a thermodynamically stable equilibrium (Choppin 1983). Pu^{3+} is usually found only in the presence of a reducing agent and would probably not be present in natural systems in appreciable quantity (Choppin 1983). Plutonium(IV) is stable in acidic solutions but tends to form polymers through hydrolysis reactions (Kobashi and Choppin 1988; Choppin 1983). The extent of Pu^{4+} polymerization increases with increasing pH (Choppin 1983). Pu^{4+} is typically removed from solution by sorption to suspended particulate matter or by gravitational settling of the larger polymers (Choppin and Stout 1989). The stability of the pentavalent form, $Pu^{V}O_2^{+}$, reaches a maximum at a pH of around 7. There is evidence that the pentavalent form may be the most stable species at the trace concentrations in most natural waters (Cleveland 1983; Orlandini et al. 1985). The hexavalent form, $Pu^{VI}O_2^{2+}$, is usually obtained in quantity through the use of an oxidizing agent such as permanganate, bromate, or persulfate (Choppin 1983). However, these trends may not hold in the presence of oxidants, reductants, or certain complexing agents.

Complexation with available ligands can have a significant impact on the sorption of Pu to surfaces by affecting the species charge and free energy of the molecule. The general affinity for complexation decreases with decreasing effective charge for each oxidation state in the following order (Choppin 1983; Kim 1986):

$$\begin{array}{ccccccc} Pu(IV)^{4+} & > & Pu(VI)O_2{}^{2+} & > & Pu(III)^{3+} & > & Pu(V)O_2{}^{+} \\ +4.0 & & +3.2 & & +3.0 & & +2.2 \end{array}$$

where the effective charge is noted below each species (Choppin 1983). The greater effective charge of $PuO_2{}^{2+}$ compared to Pu^{3+} is due to the exposure of the equatorial side of the linear O-Pu-O^{2+} molecule (Kim 1986). The general trend in the strength of the complexed species for actinides and various groundwater ligands is (Silva and Nitsche 1995):

$$OH^- \geq CO_3^{2-} > F^- > HPO_4^{-2} > SO_4^{2-} > Cl^- > NO_3^-.$$

Hydrolysis dominates most complexation reactions for Pu (further discussed below). Figure 1 shows an Eh-pH diagram for Pu in 3.6×10^{-3} *M* HCO_3^-. The modeling was preformed using Geochemist Workbench® with the Lawrence Livermore National Laboratory's thermodynamic database (Delany and Lundeen 1990). Carbonate dominates the speciation for Pu(VI) at pH values greater than about four and Eh greater than 0.5eV. Trivalent and pentavalent Pu are primarily present as free ions. $Pu(OH)_4$ is the dominant Pu(IV) species.

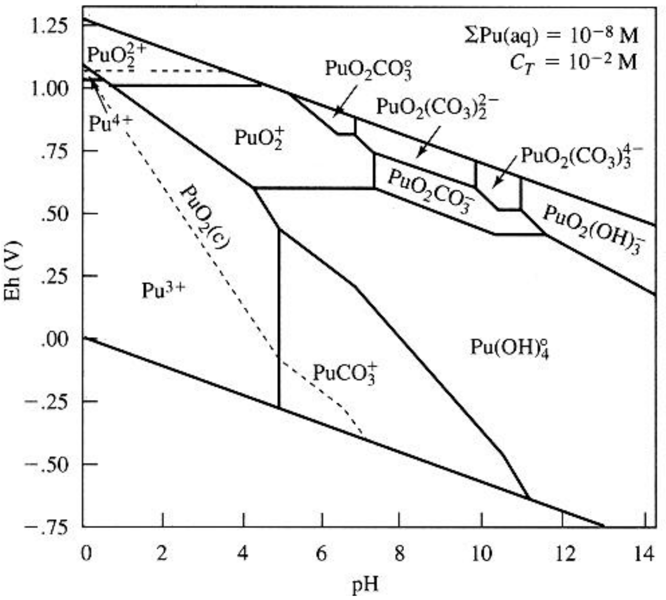

Figure 1. Eh-pH diagram of the plutonium-carbonate system at 25°C and 1 bar pressure. Dashed lines indicate the stability field of PuO_2(s) Langmuir 1997.

The dominance of these hydrolysis reactions yields a very complex chemistry for Pu even in simple solutions of varying pH and carbonate concentrations. The concentration of the free ion for each oxidation state is plotted as a function of pH for a 10^{-9} molar solution of Pu Figure 2. Hydrolysis of the Pu^{4+} ion occurs even at very low pH values and there is very little Pu^{4+} present at a pH slightly greater than one. As the pH increases the hydrolysis of other oxidation states occurs as seen in Figure 2. The effective charge of $Pu(VI)O_2^{2+}$ results in hydrolysis at a pH around 4.

The extensive hydrolysis of Pu(IV) at low pH values continues until the neutral species $Pu(OH)_4$ is formed (Figure 3) At a pH around 4.5, greater than 50% of the Pu present is $Pu(OH)_4$, which rises to greater than 99.99% around pH 7. Therefore, when performing experiments within natural pH ranges, hydrolysis reactions lead researchers to deal with $Pu(OH)_2^{+2}$, $Pu(OH)_3^{+}$, and $Pu(OH)_4$ instead of the free Pu^{4+} ion. The formation of $Pu(OH)_4$ also limits the solubility of Pu(IV) species. At Pu(IV) concentrations greater than 10^{-7} *M*, $Pu(OH)_4(s)$ precipitates as an amorphous hydroxide polymer that can be separated by ultra-filtration techniques. The amorphous polymer has been shown to form real or intrinsic colloids that significantly affect its mobility (Nelson 1987). These aggregates eventually lose a water molecule and form the PuO_2 crystalline solid that is considered to be the thermodynamically stable form of Pu (Cleveland 1979).

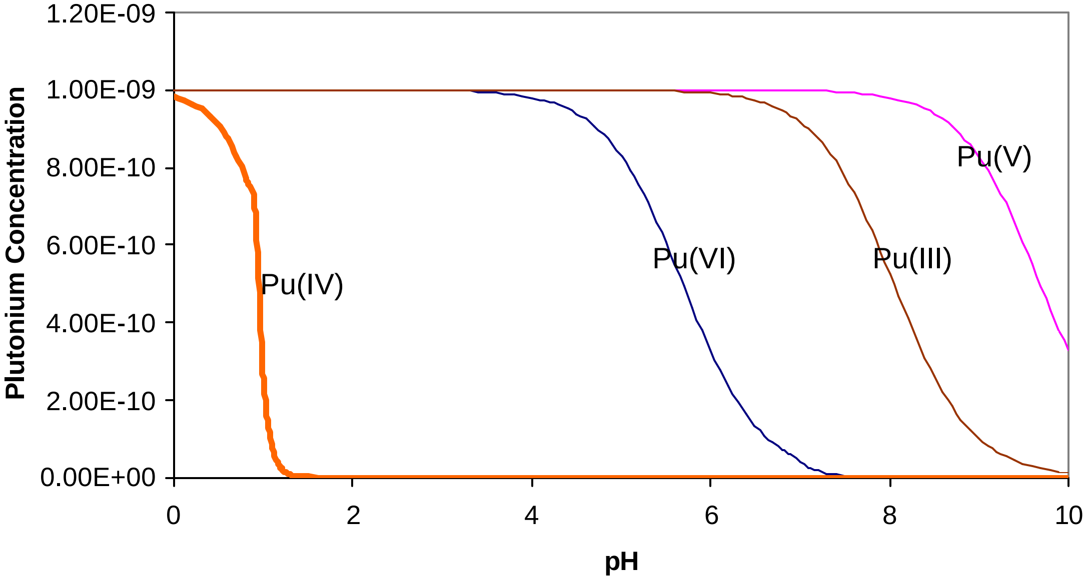

Figure 2. Free ion activity diagram for plutonium oxidation states (Geochemist Workbench LLNL Thermodynamic Constant Database; Delany et al. 1990).

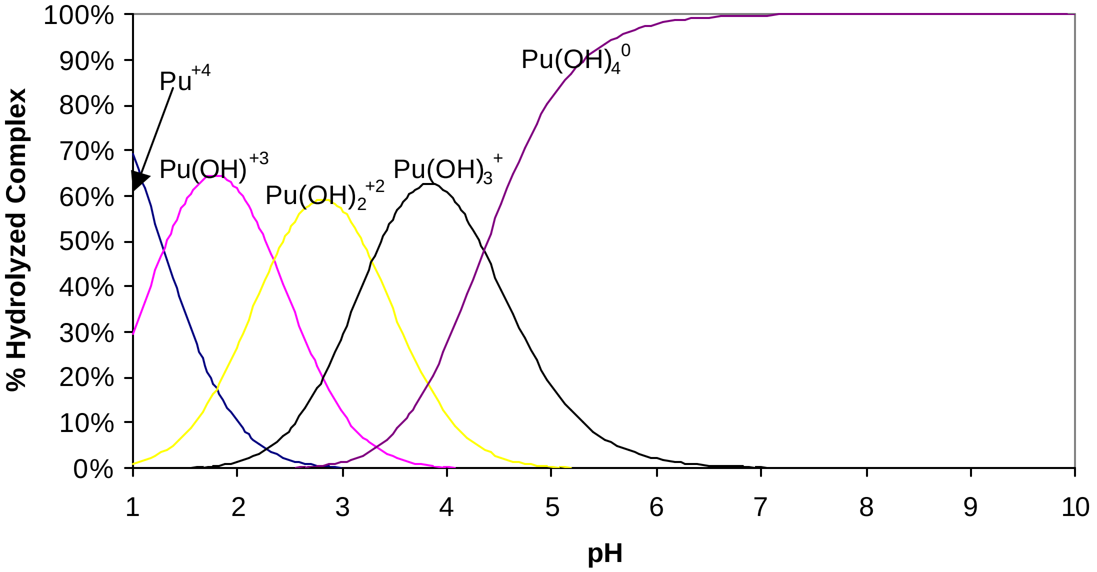

Figure 3. Pu(IV) hydrolysis versus pH (Geochemist Workbench LLNL Thermodynamic Constant Database; Delany et al. 1990).

Hydrolysis is significant at pH values typical of natural systems for all oxidation states except Pu(V) and serves to remove Pu(IV) from solution due to the strong tendency of $Pu(OH)_4$ to sorb to particles and surfaces (Choppin and Stout 1989). In all of its oxidation states, Pu cations interact with anions in solution to form ionic complexes. The general trend in both hydrolysis and complexation reaction strength is

$$Pu^{4+} \quad > \quad PuO_2^{2+} \quad \approx \quad Pu^{3+} \quad > \quad PuO_2^{+},$$

due to the respective Pu atom effective charges of +4, +3.2, +3, and +2.2 (Choppin 1983).

Plutonium solubility is limited by the formation of $Pu(OH)_4$ (Choppin 1989). Hydrolysis of Pu(IV) tends to form polymers which become more stable with age (Choppin 1989). It has been suggested that the polymers are initially formed by hydroxy bridging and are slowly converted to oxygen-bridged structures over time, thus increasing the polymeric stability. It has also been demonstrated that the polymers increase in aggregate size with increasing pH (Choppin 1989). In previous Pu sorption studies, failure to control conditions and to determine the speciation of Pu yielded Pu distribution coefficients in standardized soils that differed by three orders of magnitude among various laboratories (Cleveland et al. 1983).

Oxidation-reduction reactions may occur between the various oxidation states. The Pu(III) and Pu(IV) redox couple and the Pu(V) and the Pu(VI) redox couple are fast and reversible as both reactions involve the transfer of a single electron in each couple. The Pu(V) and Pu(IV) redox couple, however, is slow and may be very difficult to reverse because it not only involves transferring an electron to change oxidation state, but it also involves the breaking or formation of bonds with oxygen atoms (Seaborg and Katz 1954; Katz and Seaborg 1957; Capdevila et al. 1992). Redox couples such as this, involving both an oxidized form and a reduced form of Pu, usually require more energy. Capdevila et al. (1992) describes the $Pu(V)O_2^+/Pu(IV)^{4+}$ redox system as irreversible.

Disproportionation is a special type of oxidation-reduction reaction where the same molecule is both the oxidizing and reducing agent. There are several possible reactions for the various Pu oxidation states. The most important occurs when two $Pu(V)O_2^+$ atoms interact and produce a $Pu(IV)^{+4}$ and a $Pu(VI)O_2^{+2}$. The Pu(VI) is then quickly reduced to either Pu(V) or even possibly Pu(IV) (Shilov 1997; Nikitenko et al. 1995; Nikitenko & Krot 1989). Disproportionation reactions, however, are unlikely at typical environmental concentrations of Pu.

It is possible for an aqueous complexing agent or a surface to act as a catalyst to aid in the redox reaction. Oxygen, iron, manganese, nitrogen-oxides, and humic acids all can impact Pu oxidation-reduction reactions (Ahn and Nikihama 1992; Choppin et al. 1997; Duff et al. 1999; Neumoev et al. 1989). It has long been known that surfaces can catalyze chemical reactions. There are three main steps in a surface catalyzed reaction; 1) reactants adsorb onto the surface, 2) reactants react in the adsorbed state, and 3) products desorb from the surface (Srivastava 1988). The rate at which these individual reactions occur is difficult to determine and usually an overall reaction rate that includes the kinetics of the reaction, sorption, and desorption is determined (Thomas and Thomas 1967). The overall reaction rate is governed by the kinetics of the catalyzed reaction only when the surface reaction is the rate-limiting step (Clark 1970). It is often assumed that the catalyzed reaction is the rate-limiting step and the reactants and the products are in equilibrium with the liquid phase. This is known as the Langmuir-Hinshelwood mechanism (Thomas and Thomas 1967; Clark 1970).

Sanchez et al. (1985) studied the sorption of Pu(IV) and Pu(V) to goethite, α-FeOOH. In batch experiments with Pu(V) introduced in the aqueous phase, they observed the amount of Pu(IV) on the surface to increase over time. They attributed this behavior to either a disproportionation reaction, an oxidation-reduction reaction involving the iron in the goethite, or some other reaction catalyzed by the reactive surface. The reaction rate was observed to increase when the experiment was exposed to light, suggesting a possible photochemical reaction pathway. Keeney-Kennicutt and Morse (1985) obtained similar results. However, they observed both Pu(IV) and Pu(VI) being formed on the surface of goethite but further state that Pu(VI) appears to be ultimately reduced to Pu(IV).

Research by Haschke et al. (2000; 2002) at Los Alamos National Laboratory indicated that up to 27% of PuO_2 was present in an oxidized form in the presence of water. X-Ray Photoelectron Spectroscopy (XPS) analyses of the PuO_2 solid indicated the Pu was present as Pu(VI) (Haschke et al. 2000) and Extended X-Ray Absorption Fine Structure (EXAFS) spectroscopy analyses indicated that Pu was present as Pu(V) (Haschke et al. 2002). In either case, the presence of oxidized forms of Pu raises questions concerning the stability of the less-mobile tetravalent form. The proposed mechanism for this oxidation process is one of hydroxide radical production from water radiolysis followed by surface oxidation of the Pu. In the Haschke study (2002), Pu oxidation was observed in a system with a water film on pure PuO_2. We speculate that this mechanism would not be possible under environmental conditions where the Pu concentrations and associated radiolysis rates will be substantially lower. If Pu reoxidation is occurring in environmental systems, the near-field vadose zone where Pu concentration are highest and water contents are lower (presumably preventing the dilution of hydroxide free radical concentrations) is thought to be the most probable location. However, oxidation of Pu by manganese oxides has been observed in laboratory studies, where a naturally occurring manganese oxide mineral (rancieite $(Ca,Mn)Mn_4O_9$) is suspected of oxidizing Pu(IV) adsorbed to Yucca Mountain tuff (Duff et al. 1999) and Morgenstern and Choppin (2002) observed the oxidation of Pu(IV) in synthetic manganese oxide suspensions. In order to clarify modeling efforts, researchers must gain a fundamental knowledge of the Pu oxidation state transformations that may occur in the subsurface. Given that many sediments, including almost all at the SRS, contain both iron oxides and manganese oxides, possible interactions of Pu with each of these mineral phases must be elucidated.

2.2 LYSIMETERS

In the 1970's and 1980's, 115 lysimeters were installed on the SRS burial ground to study the migration of radionuclides from buried solid waste (Mersman 1982, Oblath 1984, Stone et al. 1985, Hawkins 1986). Among these lysimeters was a set of 12 minilysimeters (Hawkins 1986).[1] These minilysimeters were made from bottomless 52-liter polyethylene carboys, buried inverted at the ground surface, filled with burial ground soil, and installed to drain all percolate water from each lysimeter into its individual retention container (Figure 4). The Pu sources added to the five lysimeters used in this study are described in Table 1. The Pu sources were prepared by dissolving residual button shavings 96.5g of ^{239}Pu in 6M HCl to form a 2.6 M solution of Pu. This stock solution was used to prepare the chemical forms of Pu, and is described elsewhere (Mersman 1982). The Pu compounds were added as a few drops to a filter disc (glass fiber-reinforced paper) and the disc was sandwiched between two similar untreated discs and emplaced near the radial center of the lysimeter at a depth of 20.6 cm below the sediment surface (Mersman 1982; Hawkins 1985).

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[1] Six of the minilysimeters had different solid forms of ^{239}Pu as sources, while one contained ^{243}Am . Two minilysimeters contained radioactive ashes similar to waste generated by alpha waste incinerators. A DWPF glass pellet and waste tank sludge are also included as sources, and a control lysimeter contained no waste.

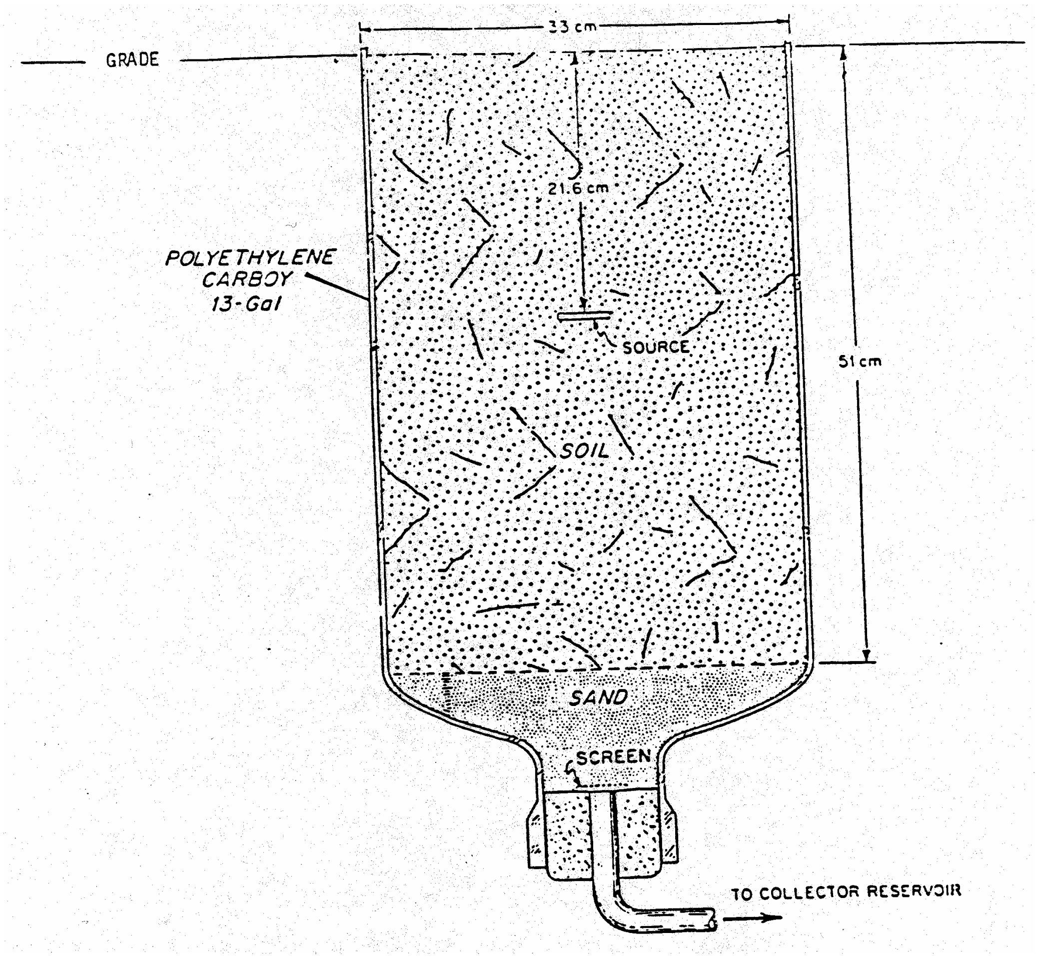

Figure 4. Schematic of lysimeter; the effluent collection reservoir is not shown.

Table 1. Lysimeter plutonium sources (plutonium added to lysimeters in November 1980).

Original Lysimeter ID	Plutonium Form	Activity
M-6	$Pu^{IV}(OH)_4$	1.47×10^9 dpm ^{239}Pu (0.7 mCi)
M-7	$Pu^{IV}(C_2O_4)_2$ (oxalate)	1.15×10^9 dpm ^{239}Pu (0.5 mCi)
M-8	$Pu^{VI}O_2(NO_2)_2$	1.06×10^9 dpm ^{239}Pu (0.5 mCi)
M-9	$Pu^{IV}(NO_3)_4$	1.17×10^9 dpm ^{239}Pu (0.5 mCi)
M-11	Control	No Pu added

Percolate water effluent first appeared in the lysimeter sumps in May 1982 (Hawkins 1985). The lysimeter effluent was monitored for $^{239/240}$Pu and ^{238}Pu on a quarterly basis until 1991 (8.91 years). These data were never published. We retrieved some of the effluent radiological analytical data from laboratory notebooks and present it, along with rainfall data, in this report.

After 11.75 years, i.e., in 1993, the lysimeters were covered to prevent rainwater infiltration. In 1994, 7.6-cm diameter cores were taken down the center of each lysimeter and then the remainder of the lysimeter facility was buried underground and covered with a geological cap to minimize rainwater infiltration. Sediment cores were stored horizontally at field-moisture conditions in Shelby tubes with plastic end caps, which in turn were double-bagged in sealed plastic bags. The cores were kept at 4°C in the dark for 9.0 years. The samples remained moist during storage. In the spring and summer of 2003, lysimeters M-6, M-7, M-9 and M-11 were removed from the 4°C climate and subsampled in a laboratory radiological area hood at room temperature, ~21°C.[2]

The sediments from the Pu(VI)-amended M-8 lysimeter [$PuO_2(NO_2)_2$; Table 1] was sampled by Hawkins (1985) in 1982, two years after the Pu source material had been buried in the lysimeter sediment. The sediment Pu concentration data generated by Hawkins were used in our transport calculations and also compared to similar data from the Pu(IV)-amended M-9 lysimeter [$Pu(NO_3)_4$; Table 1].

3.0 MATERIALS AND METHODS

3.1 LABORATORY STUDIES

There were three aspects to the laboratory studies: Sediment Characterization, Depth-Discrete Plutonium Sediment Concentrations, and Geochemical Processes Governing Plutonium Mobility.

3.1.1 Sediment and Groundwater Characterization

All lysimeters were filled with the same sediment collected from the burial grounds in E-Area, SRS. Sediment characterization was conducted with samples collected from the Control Lysimeter. Characterization was also conducted on a second sediment collected from the subsurface of the burial grounds and was used in batch Pu(IV) and Pu(V) sorption experiments to examine Pu sorption mechanisms; it was not used to parameterize subsequent modeling efforts. This second sediment, which had very similar geochemical properties as the Control, was used to preserve the Control sediment for other experiments.

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[2] The lysimeter experiment was started 21.75 years before sampling: 8.91 yr quarterly groundwater monitoring + 2.84 years left in the field without quarterly groundwater monitoring + ~1 year left covered in the field, preventing rainwater infiltration + 9 years storage in a refrigerator.

Sediment properties were measured by standard methods (Sparks 1996). Particle size distribution was measured by the sieve and pipette method; surface area by the BET N_2 sorption method; pH by the 1:1 sediment:water method; organic matter by the dry combustion method; and mineralogy by x-ray diffraction.

Groundwater was collected from an uncontaminated well located up gradient from the E-Area burial grounds. For chemical analysis, the sample was passed through a 0.45µm filter and then analyzed for pH, cations (ICP-AES), anions (IC), and total inorganic and organic carbon.

3.1.2 Depth-Discrete Plutonium Sediment Concentrations

Depth-discrete Pu sediment concentration data were successfully collected and analyzed only from lysimeter M-9, $Pu^{IV}(NO_3)_4$. The sediments from the Pu(VI)-amended M-8 lysimeter [$PuO_2(NO_2)_2$; Table 1] was sampled by Hawkins (1985) in 1982, two years after the Pu source material had been buried in the lysimeter sediment. The sediment Pu concentration data generated by Hawkins were used in our transport calculations and also compared to similar data from the Pu(IV)-amended M-9 lysimeter [$Pu(NO_3)_4$; Table 1]. Plutonium data from M-6, $Pu^{IV}(OH)_4$, lysimeter core indicated that the portion of the lysimeter containing the filter and the leachate from the filter had not been sampled. Less than 1% of the original Pu activity was in the recovered sediment. Consequently this sediment core was not used in studies to determine Pu sorption mechanisms (Section 3.1.3) or subsequent modeling (Section 4.6). The results from the depth-discrete Pu sediment concentration data from M-7, which contained $Pu^{IV}(C_2O_4(\text{oxalate}))_2$, has not been completed at this time. Consequently, there are presently no results to report for the M-7 Pu^{IV} -oxalate lysimeter.

A detailed description of how the lysimeter cores were sampled as a function of depth is included in Appendix A. A brief synopsis of the procedure follows. Cores were retrieved from the 4°C refrigerator and placed in a Radiation Area hood. The 53-cm long cores were cut into three ~18-cm segments. These core segments were then extruded in 1.25 or 2.5-cm lengths from the metal sleeves by placing in an ELE International Sample Ejector. Care was taken to sample the lower concentration Pu samples before the higher concentration samples to minimize sample cross-contamination. The sediment samples were air dried, homogenized and then sent to the Analytical Development Section at SRS for microwave digestion followed by total Pu determinations.

3.1.3 Geochemistry Processes Governing Plutonium Mobility

There were four experiments conducted using the $Pu^{IV}(NO_3)_4$ sediment to determine the important geochemical processes governing Pu mobility. The objectives of the experiments were:

- Plutonium (V) and Plutonium (IV) Sorption: Determine Pu(V) and Pu(IV) sorption to a subsurface burial ground sediment as a function of pH
- Plutonium (IV) Remobilization via Oxidation: Determine if sorbed Pu can be leached from the sediment under extreme oxidizing conditions to promote Pu desorption.
- SEM/EDX Analysis: Conduct SEM Backscattering analysis on clay particles collected from the core to look for evidence of Pu association with the clay.
- Groundwater Desorption Test: Determine desorption isotherm and Kd values from lysimeter sediments containing aged Pu

A detailed description of the materials and methods used in these experiments are presented in Appendix A. A brief synopsis of each experiment follows.

3.1.3.1 Plutonium (V) and Plutonium (IV) Sorption

The objective of this study was to examine Pu(V) and Pu(IV) sorption to a subsurface burial ground sediment as a function of pH. Each sample was prepared by adding 0.5g of sediment to a pre-weighed, acid washed polypropylene 15ml centrifuge tube. The samples were weighed again and the total mass of sediment was determined by difference. Solutions of low CO_2, $NaClO_4$ at various pH values were prepared by adding different aliquots of 0.1M $HClO_4$ 0.1M NaOH, 0.04 M $NaClO_4$, and water to achieve a final ionic strength of 0.02 within the pH range of 2 to 10. A 10mL aliquot of these solutions was added to the respective tubes. The tubes were weighed again and the total volume of solution was calculated by difference. The samples were then place on an end-over-end shaker and pH adjusted every other day with $HClO_4$ or NaOH until the pH remained stable for 48 hr (±0.1 pH units). Samples containing no soil were also prepared to evaluate sorption of Pu to the vial walls. Tubes containing sediment but no Pu spike were run in parallel to perform major ion chemical analysis of the aqueous phase.

After adjusting the sediment suspension pH, Pu(IV) and Pu(V) spikes were prepared as described in Powell et al. (2002). For Pu(V) samples, 0.125 mL of a 1547 Bq/mL spike was added for a final activity of ~15 Bq/mL. A 0.1mL aliquot of a 2100 Ba/mL Pu(IV) solution was added to each tube to give a final activity of ~21 Bq/mL. Oxidation state analysis was performed on each spike using the methods described in Powell et al. (2002).

Pu(IV) and Pu(V) were selected for this experiment because they are the predominant oxidation states in mildly oxidizing natural systems, as exists in the SRS subsurface. The aqueous phase in this experiment was selected to simplify Pu solution speciation, such that complexation would be minimized (ClO_4^- forms only very weak complexes) and hydrolysis and sediment interactions would dominate the Pu geochemistry.

3.1.3.2 Plutonium (IV) Remobilization via Oxidation

The objective of this study was to determine the extent that Pu would release from the Pu(IV) sediment, or more specifically to determine if highly oxidizing conditions could promote the release of Pu from these sediments. A detailed description of the materials and methods used in this study are presented in Appendix A. A brief description of the methods is presented here. After sectioning the $Pu^{IV}(NO_3)_4$ lysimeter, one of the lysimeter core sections with the highest Pu concentration was used in this study. 15-g aliquots of Pu-containing sediment were added to the top section of two disposable filtration units (Whatman Sterile Analytical Filter Units, cellulose nitrate membranes; Clinton, NJ). The disposable filtration units consist of two 115-mL-polyethylene reservoirs separated by a 0.22-µm membrane filter. (Typically, these units are used to filter aqueous samples, such that the sample is placed in the top 115-mL reservoir, than a vacuum is pulled beneath the filter, drawing the filtrate into the bottom 115-mL reservoir.) The sediment went through one wet – dry cycle per week. On Monday of each week 25-mL of an aerated uncontaminated SRS groundwater was added to the 15-g of sediment. On Wednesday, the water was vacuum drawn through the filter into the lower reservoir. On Thursday and Friday the soil was mixed to facilitate air drying. By the following Monday, the sediment visually appeared to be totally dry. The sediment was put through 17 wet – dry cycles. pH and Eh was measured in the sediment – water slurry on top of the filtration unit during the wet cycle. The Pu concentrations were measured in the filtrate at the end of the wet cycle.

3.1.3.3 SEM/EDX Analyses

The objective of this study was to use Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) Analysis to evaluate whether the Pu that moved in the sediment existed as discrete particles, suggesting a possible role of colloid-facilitate transport. A detailed description of the materials and methods used in this study are presented in Appendix A. Briefly, analyses were conducted on the clay-size fraction (<2-µm) of 3 sediments recovered from the M-9, $Pu^{IV}(NO_3)_4$ lysimeter and a piece of the filter (source material). The three sediment samples were 0-, 1-, and 7-cm below the filter.

3.1.3.4 Groundwater Desorption Test

The objective of this experiment was to determine a desorption isotherm using various sediments from the lysimeter that had contained $Pu^{IV}(NO_3)_4$. Isotherms are plots of containing Pu aqueous concentration data versus sediment Pu concentration data. Such plots provide some indication of the sorption processes and are also useful in contaminant transport modeling. Additionally, desorption Kd values were measured. The Pu concentrations in the sediments varied by two orders of magnitude. We were interested to learn of the trend between sediment Pu concentration and the amount of Pu desorbed, namely, were these two parameters linearly related, supportive of the Kd construct, or were they non-linear, supportive of a more complicated mechanism.

A detailed description of the materials and methods used in this study are presented in Appendix A. A brief description of the methods is presented here. Approximately 2.0g aliquots from five sediments from the $Pu^{IV}(NO_3)_4$ lysimeter were mixed with 40mL of an uncontaminated

SRS groundwater. They were left on a shaker for 1 week and then passed through a 0.22µm polycarbonate filter. The filtrate was acidified and then analyzed for total Pu.

3.2 REACTIVE TRANSPORT MODELING

The model domain is presented in Figure 5. It is selected as the vertical extent of the sediment in the lysimeter. The portion compared with the measured data is that below the Pu source (filter paper) and above the lysimeter base.

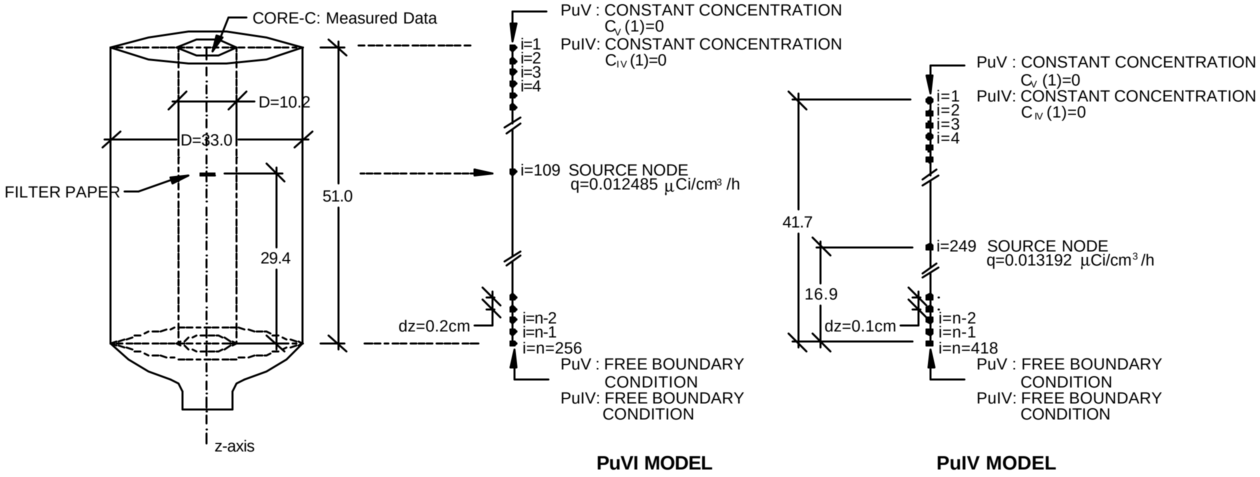


Figure 5. Lysimeter geometry and the domain of the mathematical models.

The system of equations used for the one dimensional transport of Pu(V)[3] and Pu(IV) in an unsaturated soil with a constant water content is given by:

$$R_V \frac{\partial C_V}{\partial t} = -v\frac{\partial C_V}{\partial z} + D\frac{\partial^2 C_V}{\partial z^2} - k_r(R_V - 1)C_V + k_o(R_{IV} - 1)C_{IV} \qquad (1)$$

and

---

[3] Although Pu(VI) was added to Lysimeter M-8, it is referred to through out these equations as Pu(V), the likely oxidation state that it converted to within hours to days after being added to the lysimeter.

$$R_{IV}\frac{\partial C_{IV}}{\partial t} = -v\frac{\partial C_{IV}}{\partial z} + D\frac{\partial^2 C_{IV}}{\partial z^2} + k_r(R_V - 1)C_V - k_o(R_{IV} - 1)C_{IV} \qquad (2)$$

where;

R_V, R_{IV} = Retardation factors for Pu(V) and Pu(IV)
C_V = Pu(V) aqueous concentration
C_{IV} = Pu(IV) aqueous concentration
D = Dispersion coefficient
v = Mean seepage velocity
k_r = Reduction rate constant for Pu(V)
k_o = Oxidation rate constant for Pu(IV)
θ = Mean water content

The water content was estimated as 0.3 and Pu(VI) is treated as Pu(V) in the model. Seepage velocity was calculated as v = 0.01553 cm/h for Pu(VI) and v = 0.04458 cm/h for Pu(IV), based on the measured recharge rate.

The coupled Pu(V) and Pu(IV) equations shown above were solved simultaneously by using a fully implicit finite difference scheme. Pu(V) and Pu(IV) releases from the filter papers were calculated as source terms in the governing equations at the nodes where the filters were located. Upper boundary conditions were set as zero activity concentration and lower boundaries were set to free boundary conditions for both Pu(V) and Pu(IV). Activity flux through the bottom boundary was calculated for mass balance purposes.

4.0 RESULTS AND DISCUSSIONS

4.1 SEDIMENT AND GROUNDWATER CHARACTERIZATION

Characterization of the lysimeter sediment and the sediment used in the Pu(IV) and Pu(V) Sorption Experiment (Section 3.1.3.1) is presented in Table 2. The sediments were both collected from the subsurface of the E-Area burial grounds and had similar pH, texture, and color (red). Both sediments have a relatively fine texture, typical acidic pH, and low organic matter content (although the organic matter concentrations for the lysimeter sediment were not measured, based on visual inspection of the sediment, it is likely it contains little organic matter). These types of sediments are informally referred to as "red clays," to distinguish them from the other broad category of sediments in this region referred to as "sands."

The uncontaminated groundwater used in these experiments has no unusual features compared to other region groundwater; it has extremely low salt and organic matter concentrations, and its pH is slightly acidic (Table 3).

Table 2. Sediment characterization.

Name	Description	Sand/Silt/ Clay (wt-%)	Surface Area (m^2/g)	pH	Organic Matter (wt-%)
Lysimeter Sediment	Subsurface Red Clayey Burial Ground Sediment Used to fill the Minilysimeters	NA	13.13	5.18	<0.01
Subsurface Clayey	Subsurface Red Clayey Burial Ground Sediment Low Organic Matter	58/30/12	15.31	4.55	NA

(a) Sand/Silt/Clay was measured by the sieve and pipette method; surface area by the BET N_2 sorption method; pH by the 1:1 sediment:water method; and organic matter by the dry combustion method (Sparks 1996).

Table 3. Chemical composition of uncontaminated groundwater (<0.45-µm filter).

Analyte	Units	Concentration	Method
TIC	ppm	0.713	O.I. Corp Total Organic C
TOC	ppm	0.514	O.I. Corp Total Organic C
Ag, Al, As, Be, Cd, Co, Cr, Fe, K, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Ti, U, W, Zn	ppm	BDL	ICP-AES
B	ppm	0.147	ICP-AES
Ba	ppm	0.00274	ICP-AES
Ca	ppm	0.402	ICP-AES
Cu	ppm	0.003	ICP-AES
Mg	ppm	0.287	ICP-AES
Si	ppm	3.0233	ICP-AES
Sr	ppm	0.003	ICP-AES
Li	ppb	0.209	ICP-MS
Na	ppb	154.26	ICP-MS
K	ppb	182.72	ICP-MS
Mn	ppb	1.6534	ICP-MS
Fe	ppb	0.0556	ICP-MS
Be, Cd	ppb	BDL	ICP-MS
Al	ppb	1.3927	ICP-MS
Cr	ppb	0.00489	ICP-MS
Co	ppb	0.1669	ICP-MS
Ni	ppb	0.46762	ICP-MS
Zn	ppb	3.1313	ICP-MS
Cu	ppb	18.602	ICP-MS
As	ppb	0.0816	ICP-MS
Sr	ppb	4.289	ICP-MS
Mo	ppb	0.75942	ICP-MS
Ag	ppb	0.1037	ICP-MS
Sn	ppb	0.18947	ICP-MS
Ba	ppb	8.1658	ICP-MS
Pb	ppb	1.3121	ICP-MS
Cl^-	ppm	2.6775	Bran-Lubbe Wet Chem.
NH_4^+	ppm	0	Bran-Lubbe Wet Chem.
PO_4^{3-}	ppm	<0.0012	Bran-Lubbe Wet Chem.
Total P	ppm	0	Bran-Lubbe Wet Chem.
$NO_3 + NO_2$	ppm	0.8319	Bran-Lubbe Wet Chem.
Total N	ppm	0.795	Bran-Lubbe Wet Chem.
NO_2	ppm	0	Bran-Lubbe Wet Chem.
SO_4^{2-}	ppm	<0.5556	Bran-Lubbe Wet Chem.

4.2 PLUTONIUM (VI) LYSIMETER

Plutonium sediment concentrations for the Pu(VI) lysimeter was reported by Hawkins (1985) after the $Pu^{VI}O_2(NO_2)_2$ placed in the lysimeter had been buried for two years (Figure 6). More than 90% of the Pu found in the sediment had migrated <7.5cm below the source, and most of this was within 2.5cm of the source (Table 4). About half of the Pu remained on the filter paper after two yr of leaching in the unsaturated sediment (Table 5). Furthermore, there was essentially no detectable $^{239/240}Pu$ or ^{238}Pu in the effluent leached through the lysimeter during the two year study (Hawkins 1985). Using the detection limits as the actual Pu concentration in the effluent (thus erroring on the side of overestimating the true Pu content), <0.01% of the total Pu inventory was in the effluent (Table 5). The Pu(VI) was surprisingly immobile and as will be shown in Section 4.5, is likely the result of some if not most of the Pu(VI) reducing to a less mobile form, Pu(IV).

Mass balance estimates indicate 44% of the initial Pu added is unaccounted for in either the effluent, sediment, or filter (Table 5). The cause of the poor mass balance is not known, but could be due to the fact that the core accounted for only 9.6% of the total volume of the lysimeter and perhaps analytical error. However, Hawkin's did some additional sampling of the Pu(VI) lysimeter to provide some measure of dispersion, and estimated that very little, <1% of the original activity, was not in the center 10.2cm diameter core. Thus, the rather poor mass balance reported by Hawkin's (1985) is difficult to explain.

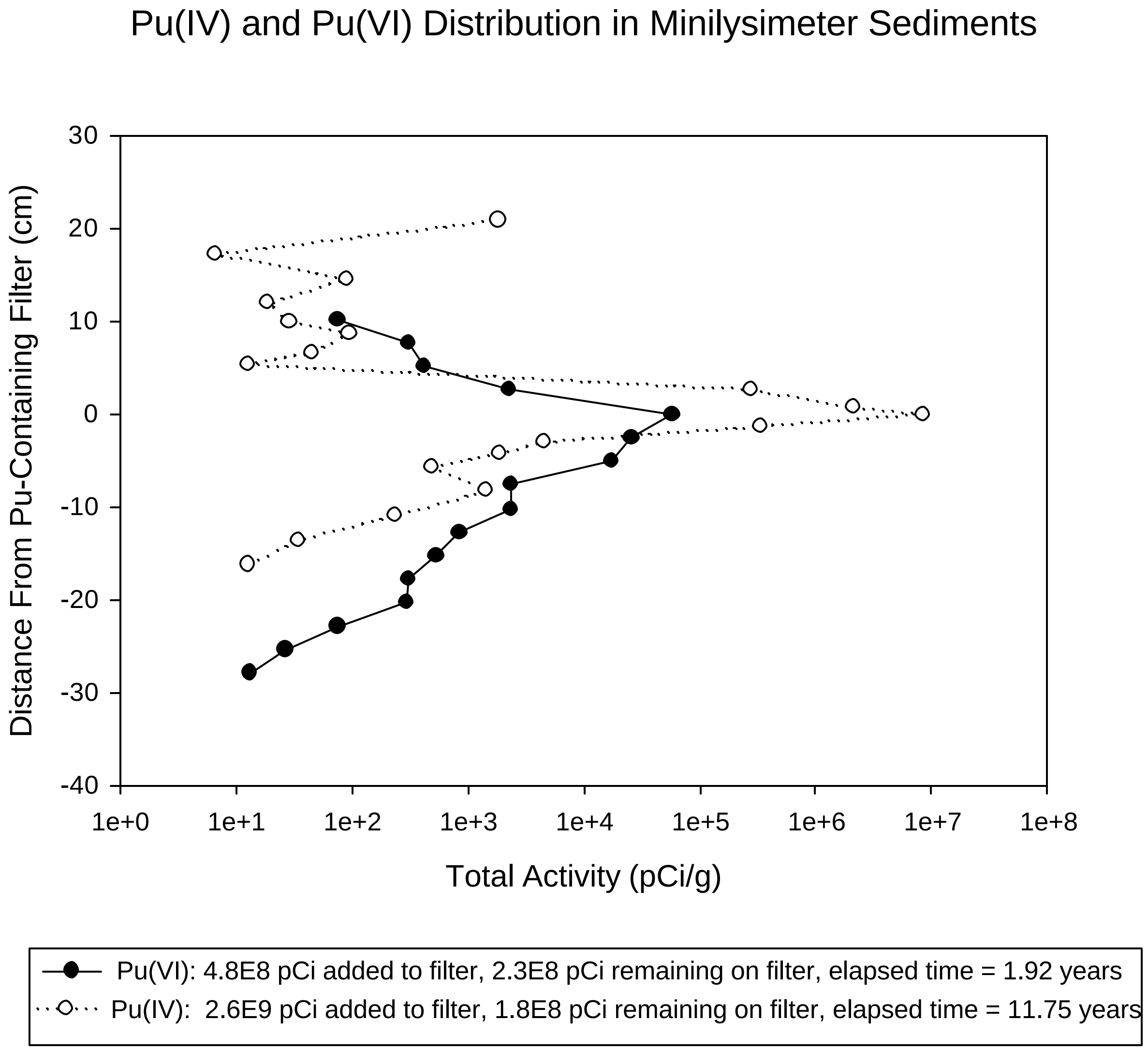


Figure 6. Total plutonium sediment concentrations after 2 years in Pu(VI) [$PuO_2(NO_3)_2$] lysimeter and after 11.75 years in the Pu(IV) [$Pu(NO_3)_4$] lysimeter.

Table 4. Plutonium concentrations in sediments collected from the lysimeter that received Pu(VI) [$PuO_2(NO_3)_2$] (data from Hawkins 1985).

Depth Below Surface – Segment Midpoint	$^{239/240}Pu$	Pu mass	% Pu in Segment
(cm)	(pCi/g)	(nCi/segment)	(%)
11.4	76.4	22	0.2
14	305	87.9	0.3
16.5	418	121	0.4
19	2250	649	2.1
21.6(a)	58400	16800	51.9
24.1	26100	7520	23.3
26.7	17500	5050	15.6
29.2	2380	686	2.1
31.8	2340	686	2.1
34.3	854	246	0.8
36.8	539	158	0.5
39.4	314	90.5	0.3
41.9	301	86.8	0.3
44.5	76.4	22	0.1
47	27	7.8	0
49.5	13.5	5.5	0
Total	111894	32238	100

(a) Filter found in this segment.

Table 5. Plutonium mass balance in the Pu(VI) [$Pu^{VI}O_2(NO_2)_2$] and Pu(IV) [$Pu^{IV}(NO_3)_4$] amended cores.

Plutonium Fraction	% of Total Pu Originally Added to Lysimeter		% of Total Pu Recovered From the Effluent, Filter, and Sediment	
	Pu(VI)	Pu(IV)	Pu(VI)	Pu(IV)
Sediment	7	36	12	87
Filter	49	7(a)	88	19(a)
Maximum Leachate(b)	<0.01	<0.01	<0.01	<0.01
Unaccounted For(c)	44	57	--	--

(a) There is a great deal of uncertainty associated with this analytical result. Only fragments of the filter were recovered. Consequently, it was necessary to estimate the fraction of the filter submitted for analysis and then multiply the analytical results appropriately to estimate the total filter Pu concentrations.

(b) There were several below-detection-values for the leachate data. These method detection limits, rather than 0 pCi/mL, were used in summing the total Pu concentration in the effluent.

(c) "The Unaccounted For" fraction includes Pu in the sediment not sampled in the core (the 10.2-cm diameter core accounted for 9.6 vol-% of the total 33-cm diameter lysimeter) and error associated with measurements, including that described in footnote (a) above.

4.3 PLUTONIUM (IV) LYSIMETER

Little Pu was detected in the effluent of the Pu(IV) lysimeter during the 8.9 years of monitoring (Figure 7; the detection limit varied from sample to sample but was generally ~1 x 10^{-3} pCi/mL). The concentrations never exceed the maximum concentration level of 0.015 pCi/mL (U.S. EPA 1991). The greatest concentrations were noted in the first 600 days. The cause of this may be due to greater colloid movement during the early period as the lysimeter sediment compacted, thereby reducing pore spaces. After 600 days, the concentrations remained at the detection limit. A new instrument was used for the last three values, i.e., after ~3000 days, and is likely responsible for the unusually high values. The cumulative rainfall data and Pu concentrations in the effluent are presented in Figure 8. As expected, the cumulative rainfall increased in a linear manner and much of the total Pu flux from the lysimeter occurred during the early part of the study.

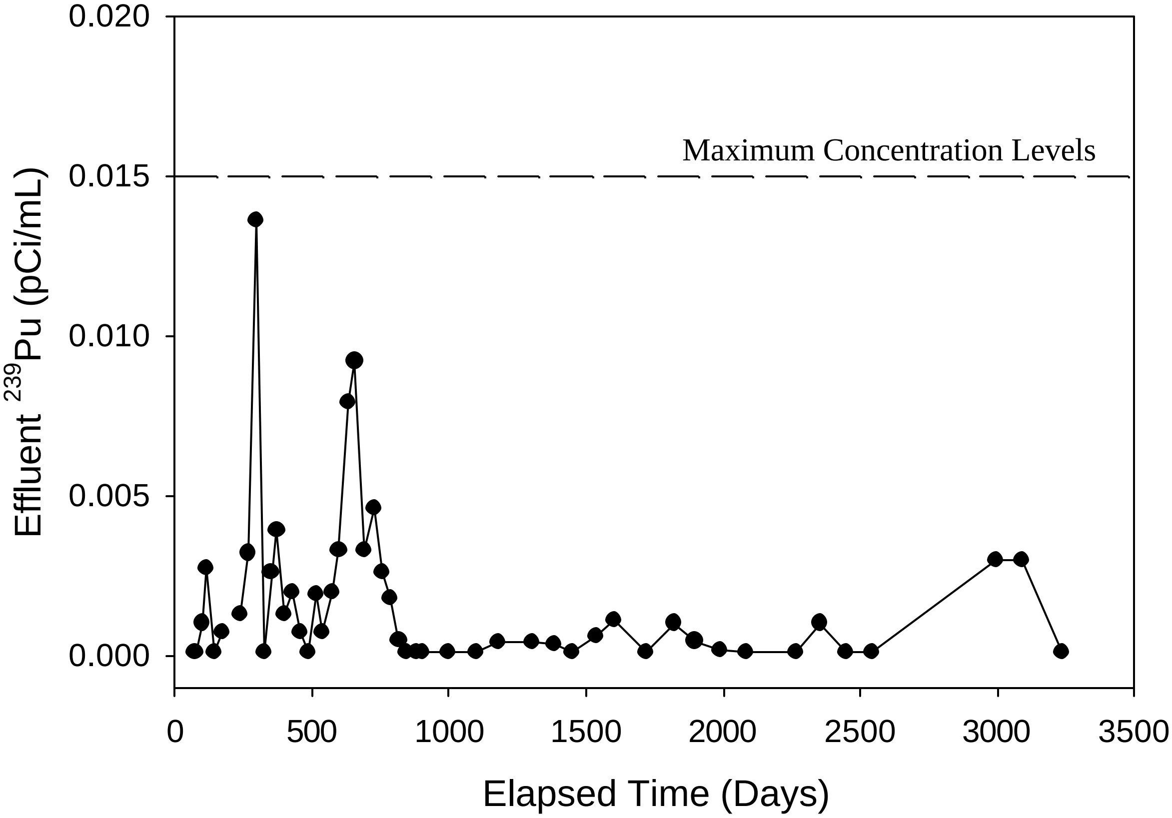


Figure 7. Plutonium-239/240 concentrations in quarterly effluent samples from the Pu$(NO_3)_4$-amended lysimeter (M-9).

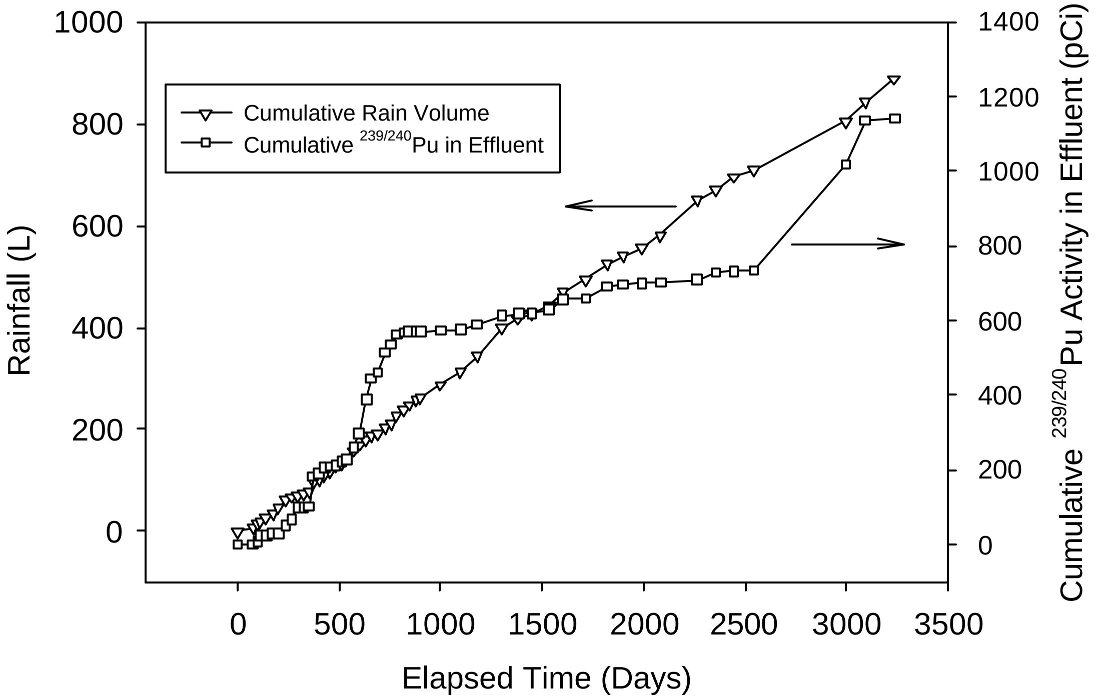


Figure 8. Cumulative rainfall and $^{239/240}$Pu effluent content from the Pu(IV) lysimeter.

Plutonium was appreciably less mobile in the $Pu^{IV}(NO_3)_4$ lysimeter than in the Pu(VI)-amended lysimeter (Figure 6). Plutonium concentration in the Pu(IV)-lysimeter core decreased 4 orders of magnitude within 5-cm of the source, whereas the Pu(VI)-amended lysimeter decreased about ½ an order of magnitude. Compounding this difference is the fact that the Pu(IV) core was leached by rainfall for four times longer than the Pu(VI) core.

Some Pu was measured in the sediment above the Pu filter, which was found in the 21.5cm depth segment (Table 6). This also occurred to a lesser extent with the Pu(VI) lysimeter (Table 4). This likely is the result of diffusion and the movement of some water due to evaporation and barometric pumping of the soil. These data will be used in future modeling work to tease out values for these two processes.

The mass balance for this core was no better than that for the Pu(VI) core (Table 5). A great deal of uncertainty is associated with the filter Pu concentration reported in Table 5 because it was determined by submitting a portion of the filter and then estimating what fraction of the entire filter the submitted sample represented. The filter was recovered as bits and pieces and was estimated to account for approximately 1/3 of the total filter.

Table 6. Plutonium concentrations in sediments collected from the lysimeter that received Pu(IV) [Pu$(NO_3)_2$].

Depth Below Surface – Segment Midpoint	$^{239/240}$Pu	$^{239/240}$Pu Mass	% Pu in Segment
(cm)	(pCi/g)	(nCi/segment)	(%)
40.4	839	252402	0.02
37.8	3.0	906	0.00
35.1	41.3	12425	0.00
32.5	8.6	2587	0.00
30.5	13.3	2001	0.00
29.2	43.7	6573	0.00
27.7	20.4	3836	0.00
26.2	5.8	869	0.00
25.2	124000	9325935	0.67
23.9	969000	218633000	15.77
21.5 (contained Pu source)	3770000	1134153989	81.83
19.5	151000	22713163	1.64
17.9	2070	467049	0.03
16.2	849	127705	0.01
14.6	220	49638	0.00
12.3	655	197048	0.01
9.6	108	32490	0.00
6.5	15.7	6494	0.00
2.3	5.8	3053	0.00
Total		1385991164	100

4.4 PLUTONIUM (IV) HYDROXIDE AND PLUTONIUM (IV) OXALATE LYSIMETERS

Sediment Pu data from M-6, the lysimeter that received $Pu^{IV}(OH)_4$, indicated that the portion of the lysimeter containing the filter and the sediment containing most of the Pu from the filter had not been recovered during lysimeter coring. Less than 1% of the original Pu activity was in the recovered sediment. $^{239/240}$Pu concentrations were equivalent to background levels and very low concentrations of ^{238}Pu were measured. This isotopic signature is difficult to explain in light of the fact that weapons-grade Pu, which consists primarily of ^{239}Pu, was used as the Pu source. The sediment concentration data is presented in Appendix B. Consequently these sediments were not used in studies to determine Pu sorption mechanisms (Section 3.1.3) or subsequent modeling (Section 4.6).

Analysis of the depth-discrete Pu sediment samples from M-7 lysimeter, which contained $Pu^{IV}(C_2O_4)_2$, (Pu-oxalate) has not been completed at this time. Consequently, no results are presented in this report.

4.5 GEOCHEMICAL PROCESSES GOVERNING PLUTONIUM MOBILITY

4.5.1 Plutonium (V) and Plutonium (IV) Sorption

For the subsurface clayey sediment (Table 2) (background soil) approximately 80% sorption of Pu(IV) occurred at pH 1.7 and greater than 95% was sorbed for pH values greater than 2.2 (Figure 9). For Pu(V), a relatively constant 20% was sorbed between pH 2 and 4. This sorption of a cationic species at low pH values could be due to a permanent negative charge present on the surface of the sediment that arises from cationic substitutions into the mineral lattice. The speciation distribution in Figure 3 indicates significant amounts of all cationic hydrolysis species of Pu(IV) that could interact with a permanent negative charge on the sediment surface. Around pH 5, Pu(V) sorption increased and by pH 6.3, more than 99% of the Pu added as Pu(V) was sorbed. After 33 days, the Pu(V) samples were analyzed again. The sorption edge shifted and were virtually identical to that of the 1 day of contact Pu(IV) data. This behavior is consistent with reduction of Pu(V) to Pu(IV). Distribution coefficients (Kd values) were calculated from the same data presented in Figure 9 and are presented in Table 7.

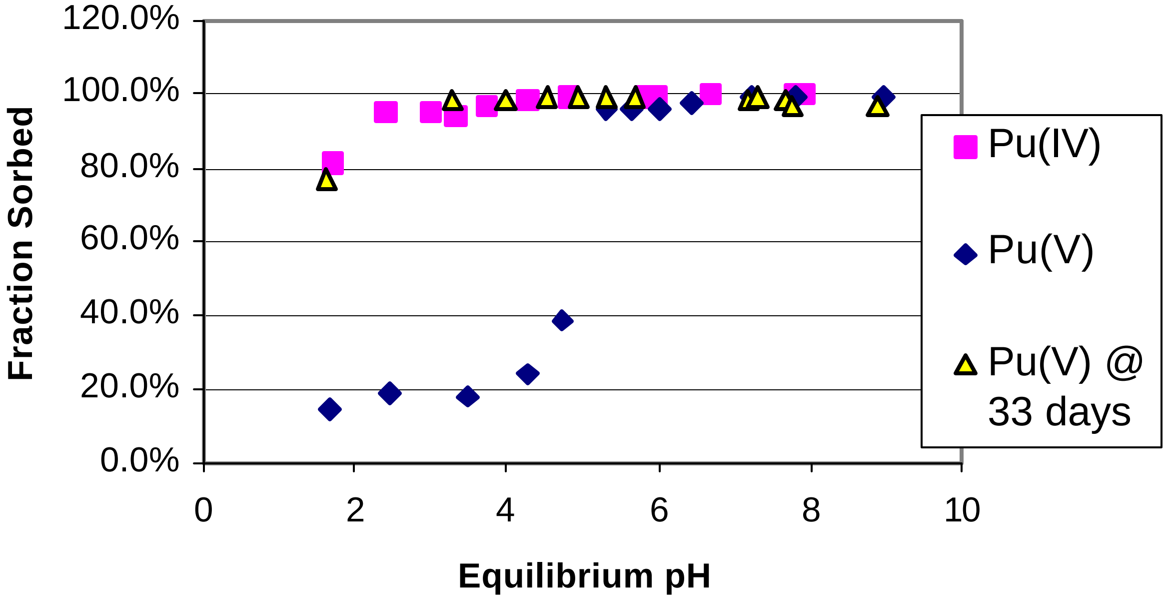


Figure 9. Pu(IV) and Pu(V) sorption edge at 1 and 33 days on the subsurface clayey sediment.

Table 7. Kd values from Plutonium (V) and Plutonium (IV) Sorption Experiment (based on the same data presented in Figure 9).

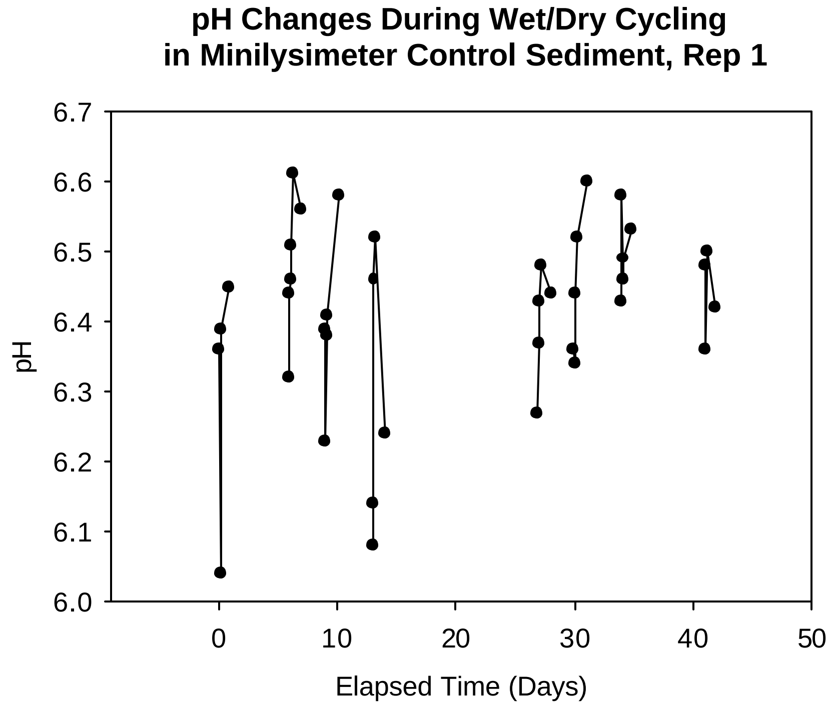
Sample Description	pH	Apparent Kd (mL/g)
Pu(IV) @ 1 day	1.71	90
Pu(IV) @ 1 day	2.39	410
Pu(IV) @ 1 day	2.98	410
Pu(IV) @ 1 day	3.34	350
Pu(IV) @ 1 day	3.74	670
Pu(IV) @ 1 day	4.26	1300
Pu(IV) @ 1 day	4.81	2100
Pu(IV) @ 1 day	5.98	9000
Pu(IV) @ 1 day	5.82	6600
Pu(IV) @ 1 day	6.68	18000
Pu(IV) @ 1 day	7.91	50000
Pu(IV) @ 1 day	7.79	42000
Pu(V) @ 1 day	1.67	4
Pu(V) @ 1 day	2.46	5
Pu(V) @ 1 day	3.50	4
Pu(V) @ 1 day	4.27	6
Pu(V) @ 1 day	4.74	10
Pu(V) @ 1 day	5.30	50
Pu(V) @ 1 day	5.63	50
Pu(V) @ 1 day	6.45	100
Pu(V) @ 1 day	6.02	440
Pu(V) @ 1 day	7.24	2300
Pu(V) @ 1 day	7.82	2600
Pu(V) @ 1 day	8.95	6600
Pu(V) @ 33 days	1.63	60
Pu(V) @ 33 days	3.28	1400
Pu(V) @ 33 days	4.00	1600
Pu(V) @ 33 days	4.53	2300
Pu(V) @ 33 days	4.95	9300
Pu(V) @ 33 days	5.32	10000
Pu(V) @ 33 days	5.68	4700
Pu(V) @ 33 days	7.16	1600
Pu(V) @ 33 days	7.32	3700
Pu(V) @ 33 days	7.69	1300
Pu(V) @ 33 days	7.74	600
Pu(V) @ 33 days	8.89	540

4.5.2 Plutonium (IV) Remobilization via Oxidation

The objective of this study was to determine if the Pu sorbed on the Pu(IV) lysimeter sediment could be desorbed from the sediment by forcing the system into more oxidized conditions. The sediments were put through 17 wet-dry cycles by adding highly aerated groundwater (~8 mg/L dissolved O_2) once a week to the sediments, removing the liquid, and then permitting the sediment to air dry. pH and Eh was measured in the sediment – water slurry on top of the filtration unit during the wet cycle. The Pu concentrations were measured in the filtrate at the start of the dry cycle.

The pH and Eh measurements during the first 8 wet - dry cycles are presented in Figure 10 and Figure 11. The pH consistently increased during any given wet cycle but did not change in a systematic manner during the course of these eight cycles. For example, the final pH of each wet cycle bounced between 6.2 and 6.6.

The Eh data was generally moderately oxidizing throughout the wet cycle. Generally, the Eh significantly decreased during the wetting cycle. During the eight cycles, the final Eh of each cycle may have gradually decreased from about 210 to 180mV. This is a small change that would not itself be expected to greatly influence the Pu oxidation states. However, not shown in these figures is the pH and Eh of the interstitial water during the drying period. During this period, it is expected that the Eh of the water increased sharply as more water was in direct contact with the air, slowly approaching 8 mg/L O_2 and an Eh of >700 mV. It is during this period that the system is expected to become greatly oxidized and to influence the oxidation state of the sorbed Pu the most.



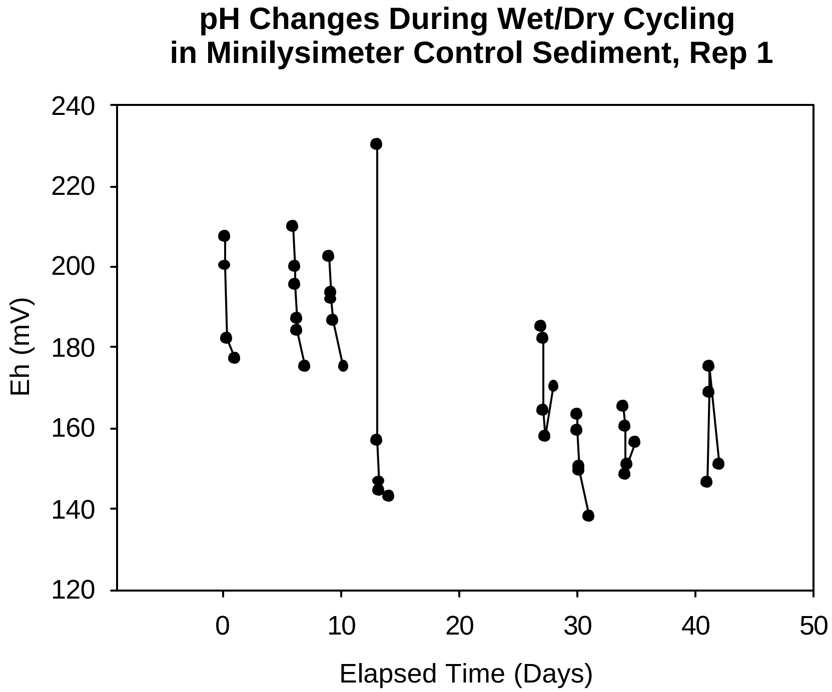
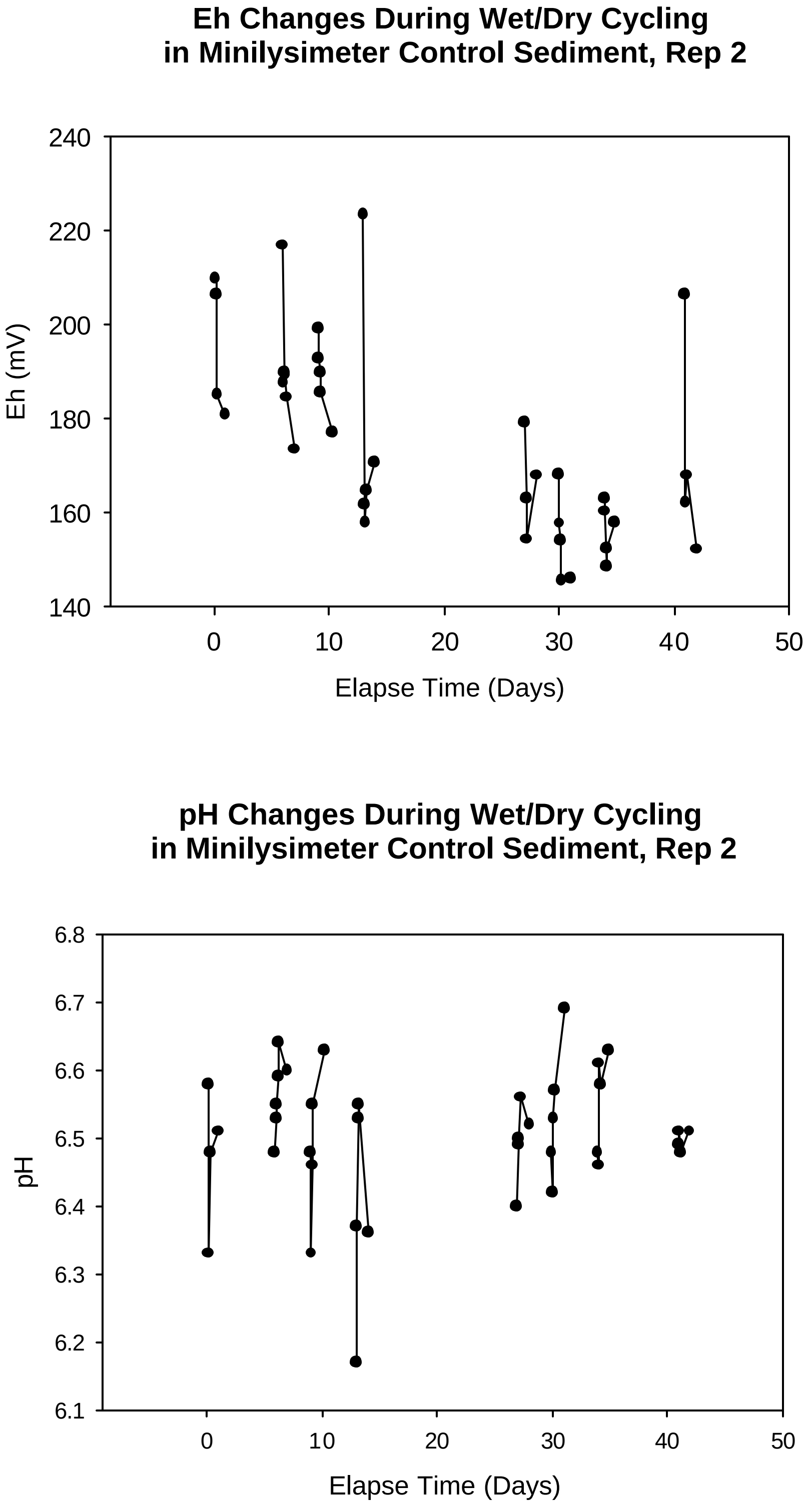


Figure 10. Eh and pH measurements of the lysimeters during the wet - dry cycling for Replicate 1.



Eh Changes During Wet/Dry Cycling in Minilysimeter Control Sediment, Rep 2

pH Changes During Wet/Dry Cycling in Minilysimeter Control Sediment, Rep 2

Figure 11. Eh and pH measurements of the lysimeters during the wet - dry cycling for Replicate 2.

The Pu concentrations in the leachate that was vacuum filtered through the sediment is presented in Figure 12. Throughout the study, Pu concentrations were quite high, much greater than the Maximum Concentration Level (MCL), 0.015 pCi/mL. This apparent inconsistent with the leachate data from the lysimeters while they were in active operation, which indicated that the Pu leachate concentrations never even approach the MCL (Figure 7). This difference may be attributed to: 1) a longer contact time between the added water and sediment, 2) a slightly more oxidized nature of the added water (>700 mV), 3) the higher solid: liquid ratio than would be expected for most moderate to high rain events, and 4) solution in contact with much higher Pu concentration than the average lysimeter concentration. None of these explanations are especially satisfying without additional experimentation to support them.

The aqueous Pu concentration in Figure 12 suggest that Pu concentrations tended to initially increase, and then to, perhaps, stabilize. A Pu concentration stabilization at 33 pCi/mL is equivalent to a fractional release of 3.23×10^{-5} $\mathrm{pCi \cdot mL^{-1}/pCi \cdot g^{-1}}$.[4] Importantly, this is a steady state, not a kinetic, construct. It is likely that the underlying reaction responsible for the trend in Figure 12 is oxidation of sorbed Pu(IV) because during a preliminary experiment in which the water was not first aerated, very little Pu was detected in the leachate (Figure 13). More work is necessary to confirm whether oxidation is in fact the mechanism responsible for the Pu release from the sediment. This preliminary study was conducted simply to determine whether aeration was necessary to observed Pu release from the sediment; it was not replicated. Table 8 expresses the data in this figure as apparent Kd values and solubility. The extremely high apparent Kd values likely reflect that fact that the system had not come to equilibrium during the 2 day contact time (hence the adjective "apparent"). The apparent solubility values were in the order of 10^{-9}M, which is higher than that expected for $\mathrm{PuO}_{2\,amorph}$, which has a solubility value in the order of 10^{-14}M. These relatively high solubility values may in part be attributed to the short contact time and also to the presence of Pu solids inadvertently passing through the 0.22-µm filter used to sediment from the liquids from the solids in these samples.

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[4] (33 pCi/mL x 25 mL)/(1.70E06 pCi/g soil x 15 g) = 3.23E-05 $\mathrm{pCi \cdot mL^{-1}/pCi \cdot g^{-1}}$

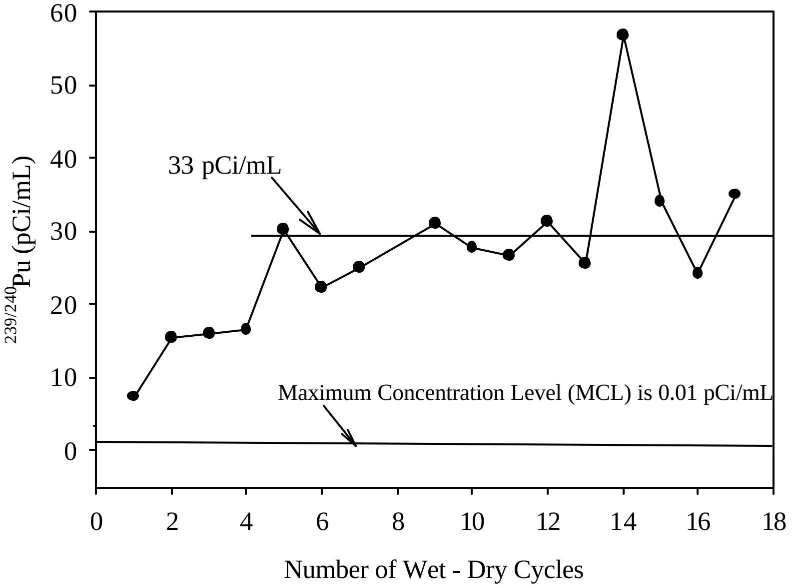


Figure 12. Aqueous plutonium concentrations during 17 weekly wet - dry cycles imposed on a Pu(IV) lysimeter sediment.

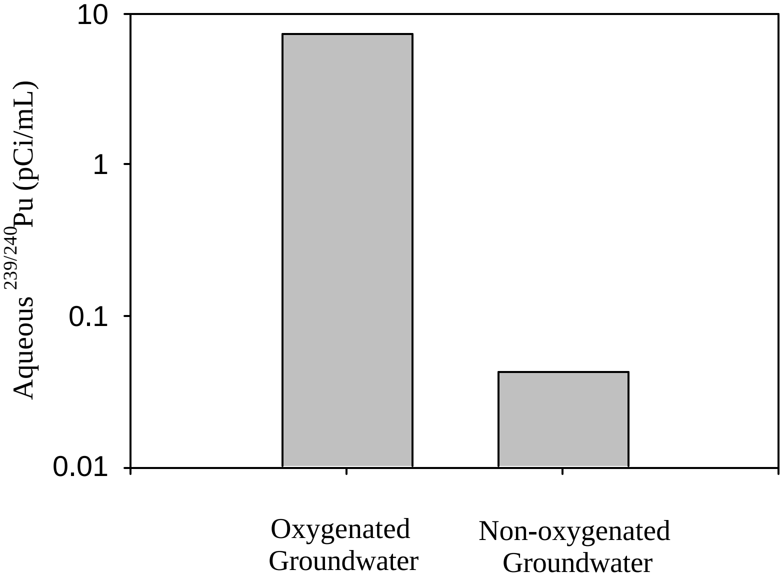


Figure 13. Plutonium desorption from a Pu(IV)-amended lysimeter sediment in an aerated and non-aerated SRS groundwater (sediment went through one wet – dry cycle).

Table 8. Desorption apparent Kd values and solubility values from the Wet - Dry Cycling Experiment.

Cycle Number	Kd ^{238}Pu	Kd $^{239/240}$Pu	Solubility $^{239/240}$ Pu
	(mL/g)	(mL/g)	(M)
1	BDL	231288	5.0E-10
2	BDL	110557	1.0E-09
3	BDL	107102	1.1E-09
4	BDL	102725	1.1E-09
5	51206	56353	2.0E-09
6	BDL	76162	1.5E-09
7	75920	68051	1.7E-09
9	55969	54638	2.1E-09
10	62241	61401	1.9E-09
11	59180	63682	1.8E-09
12	46883	54401	2.1E-09
13	58699	66608	1.7E-09
14	26350	29921	3.8E-09
15	53881	49934	2.3E-09
16	55969	70205	1.6E-09
17	51942	48520	2.4E-09

(a) 15-g sediment #228 (collected just beneath filter in $Pu^{IV}(NO_3)_4$ combined with 25-mL SRS groundwater, contact time 2 days.

4.5.3 SEM/EDX Analyses

The objective of this study was to use Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) Analysis to evaluate whether the Pu that moved in the sediment existed as discrete particles, suggesting a possible role of colloid-facilitate transport. Analyses were conducted on the clay-size fraction (<2-µm) of 3 sediments recovered from the M-9, Pu(IV) lysimeter and a piece of the filter recovered from the lysimeter. The sediment samples were collected from 0-, 1-, and 7-cm below the filter. It is important to note that this is not an especially sensitive method for detecting such colloids because it requires percent levels of an element for detection. As such, it would essentially only detect Pu in particles that Pu was one of the primary elements in the precipitate and would likely not detect particles that Pu simply adsorbed onto.

Plutonium was detected only on the filter or on sediment particles located within ~0.25cm from the filter. Plutonium was not detected in sediment samples 1 and 7 cm below the filter. An image of the filter shows the three dimensionality of the material (Figure 14). Because the Pu was added to a filter that was sandwiched between two other filters, it was necessary to collect data from the outside filters and the inside filters. The latter required that we separate the filters, a task that was made difficult by the fact that the filters did not separate easily. Figure 14 is an image of the outside filter that did not directly receive the aqueous $Pu^{IV}(NO_3)_4$. The Pu-bearing particles detected on the filter, both on the outside and inside layers, were abundant, existing in almost every image taken at 1000x (Figure 15). These particles are labeled in Figure 15 as "B" and confirmation that percent concentrations of Pu existed in the particles was obtained through EDX analysis of the "B" particles (Figure 16). The Pu particles were very easy to identify when the SEM was set to backscatter electron mode. In the backscatter mode, the Pu particles would be much brighter than the other minerals, an indication, loosely speaking, that the particles had a higher density. These particles were 1.5 to 4 cm in diameter. The EDX spectra of the "B" particles were very consistent and always included a large Al, Si and Fe peak. These elements may be part of the Pu-bearing particle or may be part of nearby particles, since it is very likely that the x-ray beam hit more than one particle.

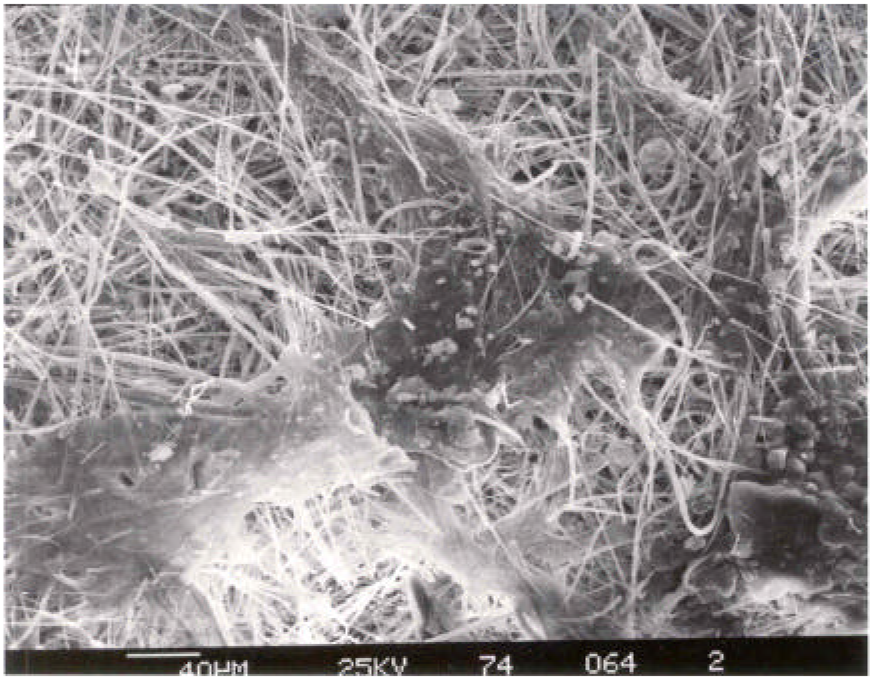


Figure 14. SEM image of filter recovered from the Pu(IV) lysimeter (reference bar is ~40 µm).

Figure 15. SEM images of particles on filter recovered from the Pu(IV) lysimeter. “B” particles contained high concentrations of Pu (in top image the reference bar is ~10 µm.; bottom image it is ~2µm).

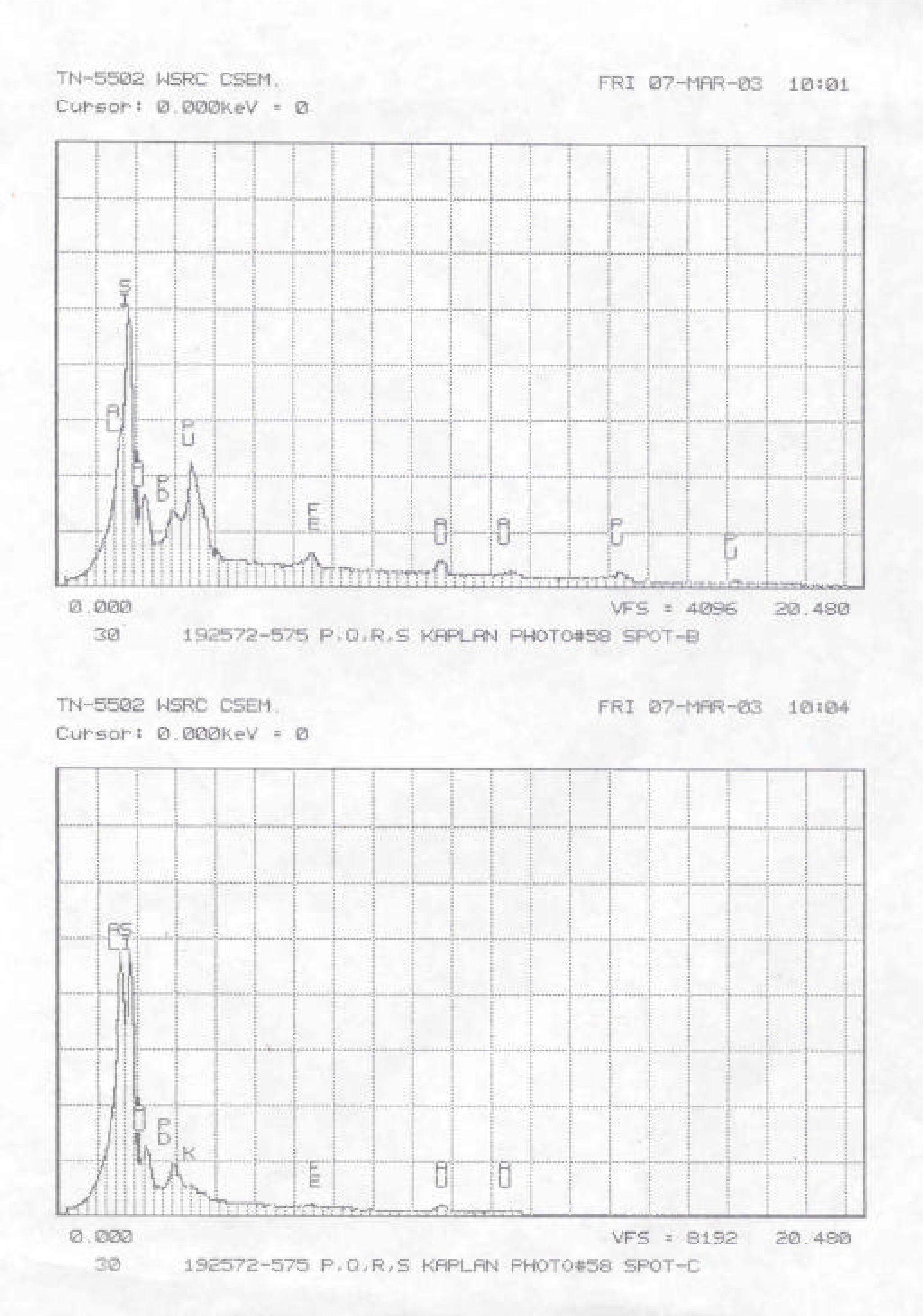


Figure 16. Energy Dispersive X-Ray (EDX) analysis spectra of: Top - Pu-bearing particles, and Bottom - an example of a very common spectra of an aluminum silicate mineral containing iron.

4.5.4 Groundwater Desorption Test

The objective of this experiment was to determine a desorption isotherm using various sediments from the lysimeter that had received $Pu^{IV}(NO_3)_4$. Isotherms are plots of aqueous Pu concentration versus sediment Pu concentration data. Such plots provide some indication of the sorption processes and are also useful in contaminant transport modeling. Additionally, apparent desorption Kd values were measured. Four sediments from the Pu(IV) lysimeter were brought to equilibrium with groundwater for 7 days and then the aqueous Pu concentration were measured. Solid phase Pu concentrations at equilibrium were calculated by subtracting the amount desorbed into the aqueous phase from the amount originally in the sediment.

The desorption isotherm is presented in Figure 17. As expected, the more Pu in the sediment, the more that went into the aqueous phase. The data is clearly not linear, indicating a Kd construct would not be appropriate for the entire range of aqueous Pu concentrations tested. However, the curve does not follow a Freundlich or Langmuir response or a precipitation trend either. This stems from the non-classical observation that the curve increases in slope at higher Pu concentrations with a larger fraction of the Pu being transferred to the aqueous phase for the higher total Pu concentrations. Possible explanations for this observation include: (1) Pu in the less concentrated has been transformed into a less available form during transport from the filter (e.g., $Pu^{IV}(NO_3)_4$ to $Pu^{IV}(OH)_4$); and/or (2) mass transfer limitations prevent equilibrium from being established for the lower concentration samples (e.g., coprecipitation of Pu with Fe/Mn oxides during transport). Kd value are presented in Table 9 and range from 2700 to 92,000 mL/g. Such a wide range compromises the use of this construct to represent all sorption processes across this Pu concentration range. These values are generally lower than those reported from the Wet – Dry Cycling Experiment (Table 8) because there was a longer desorption period to permit greater Pu to desorb. Additional data from this experiment is presented in Appendix C.

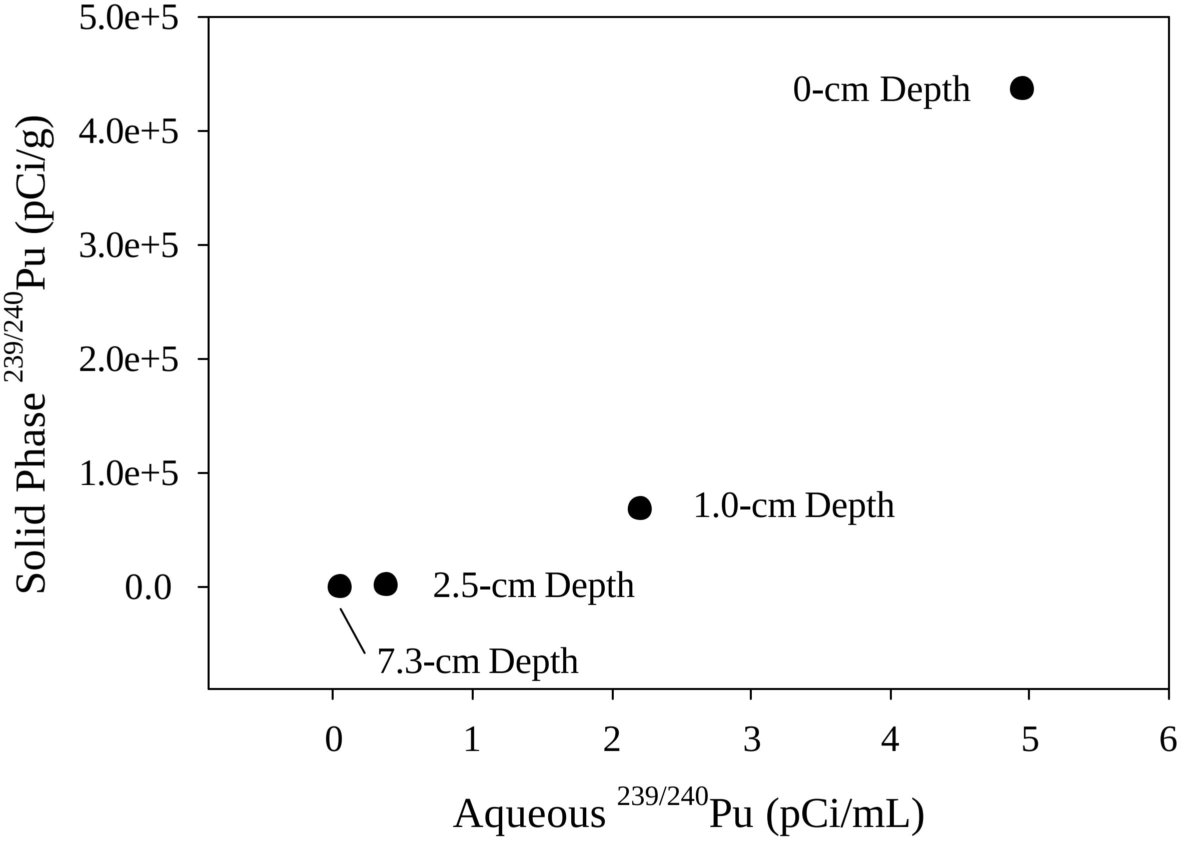


Figure 17. Desorption isotherm showing solid phase and aqueous $^{239/240}$Pu concentrations after 1 week equilibration of uncontaminated SRS groundwater and 4 Pu(IV) lysimeter sediments. (average of 3 observations, error bars are smaller than symbol). Depth of sample below filter also shown

Table 9. Desorption aqueous and solid phase $^{239/240}$Pu concentrations and apparent Kd values.

Effluent $^{239/240}$Pu	Sediment $^{239/240}$Pu	Kd
(pCi/mL)	(pCi/g)	(mL/g)
0.055 ± 0.019	294 ± 0	4802 ± 1406
0.377 ± 0.142	925 ± 3	2711 ± 968
2.209 ± 0.282	67974 ± 6	31162 ± 4300
4.952 ± 1.381	436387 ± 28	92378 ± 22792

4.6 REACTIVE TRANSPORT MODELING

The retardation values used in the simulations are based on the laboratory sorption experiments described in Sections 4.5.1 and not from the desorption experimental data described in Section 4.5.4. The reduction rate values, k_r, were either based on previous laboratory work done on SRS sediments (Fjeld et al. 2003) or were treated as an adjustable parameter. Oxidation rate input values, k_o, were always treated as an adjustable parameter.

Figure 18 shows modeling results from the Pu(VI) lysimeter where the retardation values were fixed and the oxidation and reduction rate constants varied. Simulation #1 shows that by assuming no reduction (i.e., k_r is set to 0 hr^{-1}), that the depth Pu is expected to migrate is greatly overestimated. Conversely, Simulation #2 shows that when all the Pu(VI) is rapidly reduced to Pu(IV) (i.e., k_r is set very fast, 1×10^{-2} hr^{-1}), then the depth that the Pu is expected to migrate is greatly underestimated. By including a more moderate reduction rate of 2×10^{-4} hr^{-1} in Simulation #3, we obtain a better fit. This reduction rate agrees reasonably well with the measured value reported by Fjeld et al (2003) for a sandy textured SRS sediment, 4×10^{-3} hr^{-1}. By including a slow oxidation rate in Simulation #4, there is no discernable improvement in the model prediction.

Figure 19 shows the modeling results from the Pu(IV) lysimeter after 21.75 years (after it had been exposed to rainfall for 11.75 years and left in storage for 10 years; see footnote[2] on page 9). Simulation #1 shows that by assuming no oxidation of Pu(IV) took place that the model greatly underestimates the depth that Pu traveled. In Simulations #2 and #3, oxidation rates were varied and no subsequent reduction was permitted to occur. The shapes of these curves do not capture the important features of the data, and as such, are not considered accurate representations of the data. Simulation #4 through #7, vary the oxidation and reduction rates. Simulation #7 represents the best fit with an oxidation rate, k_o, of 1.0×10^{-8} hr^{-1}, and a reduction rate, k_r, of 1.2×10^{-3} hr^{-1}. The reduction rate is near identical to that measured by Fjeld et al (2003) for a sandy textured SRS sediment, 4×10^{-3} hr^{-1}. Based on simulation conducted for 21.75 years (Figure 19) and 11.75 years (Figure 20), very little movement of Pu occurred while the core samples were in cold storage for 10 years. The main impact of letting the samples sit for 10 years in cold storage on Pu distribution was that it made changes in the Pu concentration profiles less sharp, i.e., changes in Pu concentrations with depth were slightly less different.

An important conclusion from this work is that the 10^{-8} hr^{-1} oxidation rate used in Figure 19 and Figure 20 is an extremely slow reaction rate, yet it greatly improved the model fit.

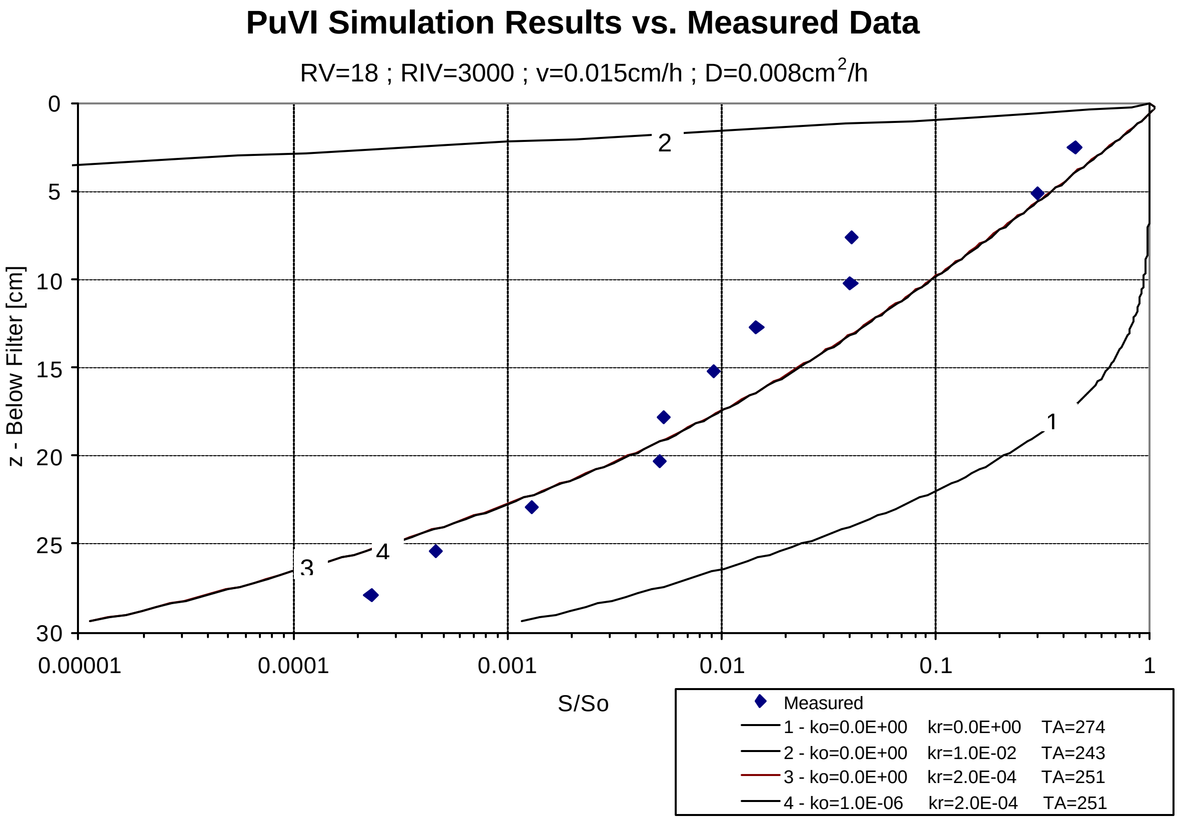
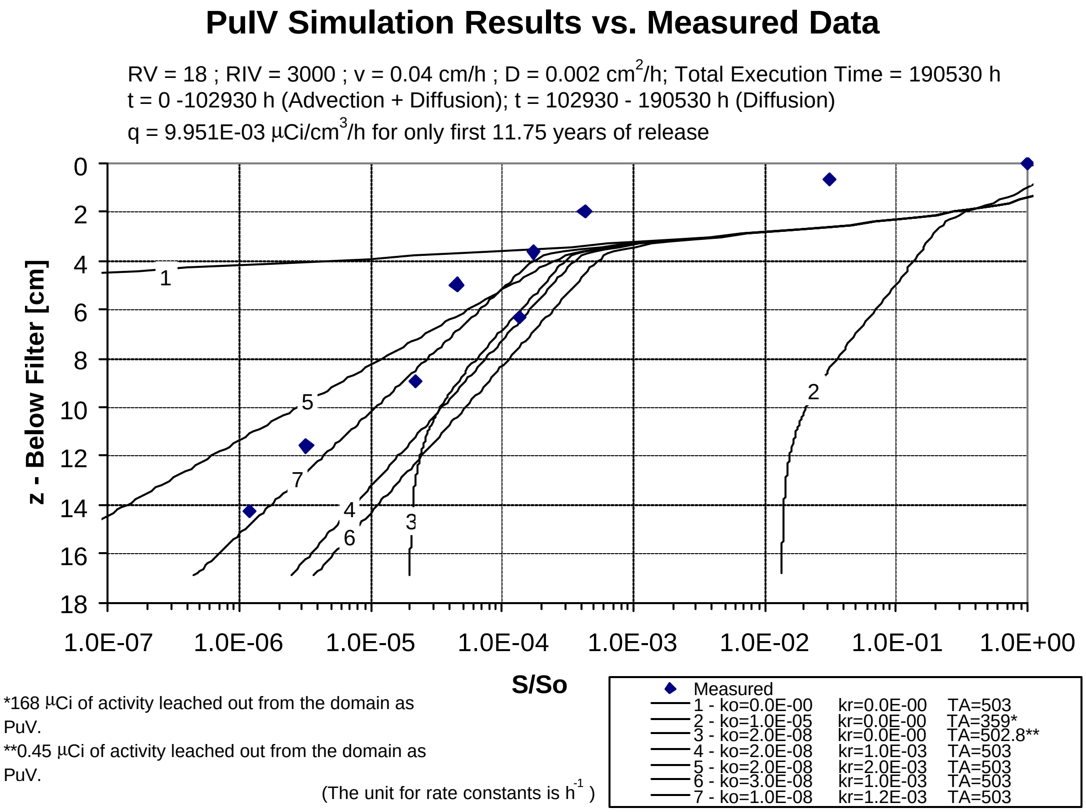


Figure 18. Simulations of the Pu(VI) lysimeter sediment data. (S/So = normalized sediment Pu concentrations, RV = retardation factor for Pu(V), RIV = retardation factor for Pu(IV), v = water velocity, D = dispersion, ko = first order rate constant for Pu(IV) oxidation to Pu(V/VI), kr = first order rate constant for Pu(V/VI) reduction to Pu(IV), TA = total activity in model domain).



*168 µCi of activity leached out from the domain as PuV.

**0.45 µCi of activity leached out from the domain as PuV.

(The unit for rate constants is h^{-1})

Figure 19. Simulations of the Pu(IV) lysimeter sediment data. (Simulation duration = 21.75 years = 11.75 years of advection and diffusion = 10 years diffusion (sample core in storage), S/So = normalized sediment Pu concentrations, RV = retardation factor for Pu(V), RIV = retardation factor for Pu(IV), v = water velocity, D = dispersion, ko = first order rate constant for Pu(IV) oxidation to Pu(V/VI), kr = first order rate constant for Pu(V/VI) reduction to Pu(IV), TA = total activity in model domain).

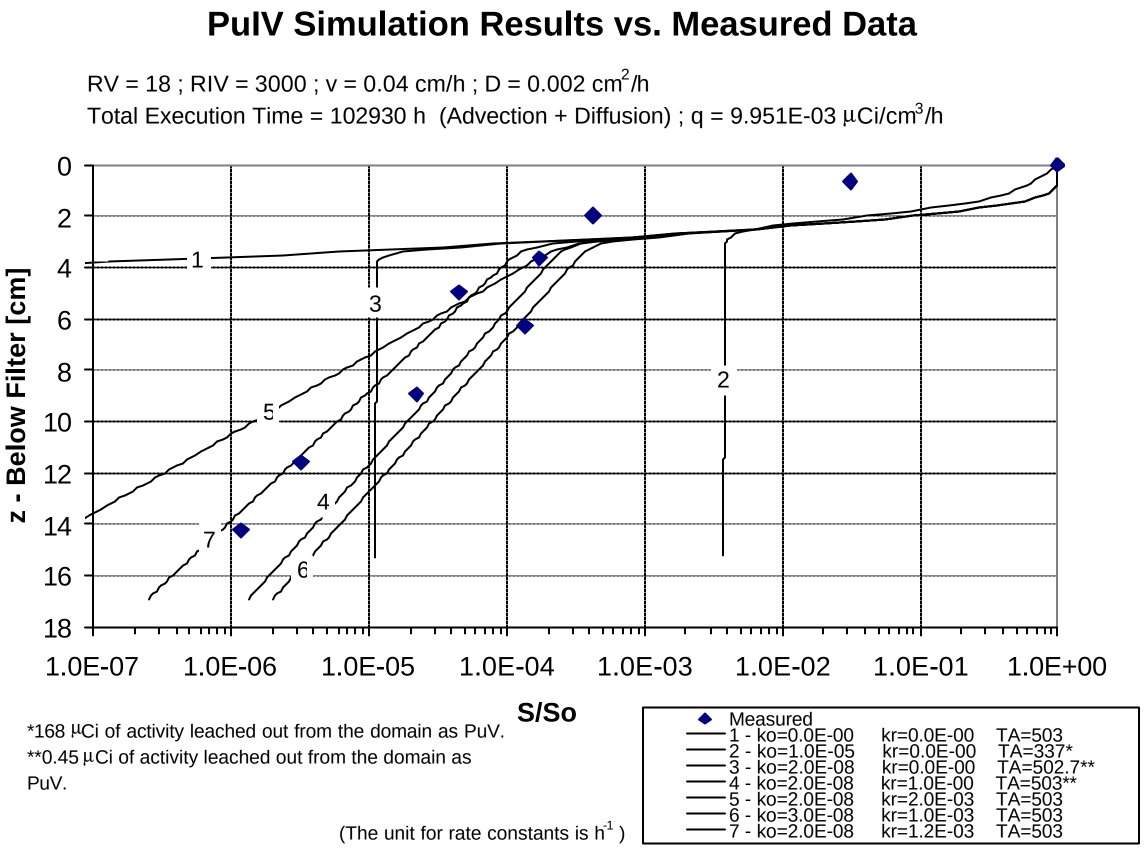


Figure 20. Simulations of the Pu(IV) lysimeter sediment data. (Simulation duration = 11.75 years; all else similar to Figure 19).

5.0 CONCLUSIONS

Plutonium migration through the lysimeter sediments could not be adequately described by the common advection-dispersion equation, where the chemical reaction term is defined by a simple Kd adsorption model. Instead it was shown that the oxidation state of the Pu was a key parameter and that the oxidation state likely changed during the 2 or 9 year studies. When Pu was placed in the lysimeter as Pu(VI), the Pu(VI) likely reduced to Pu(V) where it moved through the sediment relatively quickly. The Pu(V) in turn became immobilized once it was further reduced to Pu(IV). Transport modeling indicated that most of the Pu would have leached out of the sediments had the Pu remained in the form of Pu(VI). Additionally, laboratory studies showed that Pu(VI) quickly converted to Pu(V) in groundwater simulants without sediment (data not presented). Once Pu(V) was added to SRS sediments, the Pu sorbed relatively weakly after one day of contact, but after 33 days of contact, the Pu(V) sorbed much stronger to the sediment and in a manner identical to that of Pu(IV).

Plutonium mobility was appreciably slower in the lysimeter that received Pu(IV) than Pu(VI). There were two pieces of evidence that some Pu(IV) likely oxidized to Pu(V/VI) during the 8.9 years experiment. Laboratory studies showed a measurable concentration of Pu entering into the mobile phase once oxygenated groundwater was added to it in a wet – dry cycling pattern, non-oxygenated water did not result in the desorption of nearly as much Pu. The second indication that some oxidation occurred in the systems came from our transport modeling. If no oxidation of Pu(IV) was permitted in the simulation, the model underestimated Pu mobility. Upon including a small oxidation rate, it was possible to capture the important features of the data set.

In conclusion, these studies suggest that Pu is extremely immobile in the SRS subsurface environment. The reason for this is that oxidized Pu(V/VI) will quickly, within a month of entering the sediment environment, be reduced to the less mobile form of Pu(IV). The Pu(IV) is essentially immobile in SRS sediment, sorbing at least two orders of magnitude greater than Pu(V). However, a small fraction of Pu(IV), 3 x 10^{-5}(pCi Pu·mL^{-1})/(pCi Pu·g^{-1}), converts to Pu(V), making it possible to observe trace amounts in the aqueous phase when the Pu is added to the system as Pu(IV).

The lysimeter results provide important long-term data that support the removal of important overly conservative approaches presently used to calculate risk and performance assessment associated with groundwater Pu. These findings have significant implications to existing SRS programs, including the Pu Immobilization, LLW Disposal, and Remediation of the Old Burial Ground, and future SRS programs, including MOX and pit disassembly.

6.0 REFERENCES

Ahn, J.; S. Nakayama, (1992) “Modeling for migration of a redox-sensitive radionuclide in engineered barriers,” *Nuclear Technology*. 97, 323-335

Bondietti, E. A., (1982) “Mobile Species of Pu, Am, Cm, Np, and Tc in the Environment,” IAEA-SM-257/42, International Atomic Energy Agency, Vienna.

Bryan, N.D.; F.R. Livens; A.D. Horrill, (1994) “Biogeochemical behaviour of plutonium and americium and geochemical modelling of the soil solution,” *Journal of Radiological and Nuclear Chemistry*. 182, 359-366.

Capdevila, H.; P. Vitorge; E. Giffaut, (1992) “Stability of pentavalent plutonium,” *Radiochimica Acta*. 58/59, 45-52

Choppin, G. R., (1983) “Aspects of plutonium chemistry,” *Radiochimica Acta* 32, 43-59.

Choppin, G. R.; B. E. Stout, (1989) “Actinide behavior in Natural Waters,” *Sci. Total Environ.*, 83, 203-216.

Choppin, G.R.; A.H. Bond; P. M. Hromadka, (1997) "Redox speciation of plutonium," *J. Radiological and Nucl. Chem.* 219, 203-210.

Clark, A., (1970) *The Theory of Adsorption and Catalysis*. Academic Press. New York.

Cleveland, J. M.; Rees, T. F.; Nash, K. L., (1983) "Groundwater Composition and its Relationship to Plutonium Transport Processes," American Chemical Society.

Clevland, J.M. (1979) *The Chemistry of Plutonium* p. 651. American Nuclear Society, La Grange Park, IL.

Cook, J. R., (2002) "Special Analysis, Effect of New Plutonium Chemistry on SRS Trench Disposal Limits," WSRC-TR-2002-00154, Savannah River Technical Laboratory, Aiken, SC.

Delany, J.M.; Lundeen, S.R., "The LLNL Thermochemical Database", Lawrence Livermore National Laboratory Report UCRL-21658, 150 p., 1990.

Duff, M. C.; D. B. Hunter; I.R. Triay; P. M. Bertsch; D.T. Reed; S.R. Sutton; G. Shea-McCarthy; J. Kitten; P. Eng; S. J. Chipera; D. T. Vaniman, (1999) "Mineral associations and average oxidation states of sorbed Pu on tuff," *Environ.Sci.Technol.* 33, 2163-2169.

Fjeld, R. A.; S. M .Serkiz; P.L. McGinnis; A. Elci; D.I. Kaplan, (2003) Evaluation of a conceptual model for the subsurface transport of plutonium involving surface mediated reduction of Pu(V) to Pu(IV). *J. Contaminant Hydrology* (In Press).

Haschke, J.M.; Allen T.H.; Morales L.A., (2000) "Reaction of plutonium dioxide with water: Formation and properties of PuO_{2+x}," *Science*, 287, 285-287

Haschke, J.M.; Allen, T.H., (2002) "Equilibrium and thermodynamic properties of the PuO2+x solid solution," *J of Alloy and Comp.* 336, 124-131.

Hawkins, R. H., (1985) "Soil Coring in a Plutonium Wasteform Lysimeter," DPST-84-481, Westinghouse Savannah River Company, Aiken, SC.

Hawkins, R. H., (1986) "Lysimeters for Waste Migration Studies at the SRP Burial Ground," Memorandum to J. A. Stone, February 14, 1986, Westinghouse Savannah River Company, Aiken, SC.

Hooker, R. L., and Root, R. W., (1981) "Lysimeter Tests of SRP Waste Forms," DP-1591, Westinghouse Savannah River Company, Aiken, SC.

Katz, J.J.; G.T. Seaborg, (1957) *The Chemistry of the Actinide Elements*. John Wiley & Sons Inc. NY.

Keeney-Kennicutt, W.L.; J.W. Morse, (1985) "The redox chemistry of Pu (V)O_2^+ interaction with common mineral surfaces in dilute solutions and seawater," *Geochimica et Cosmochimica Acta*. 49, 2577-2588.

Kim, J. I. (1986) "Chemical Behavior of Transuranic Elements in Natural Aquatic Systems," *Handbook on the Physics and Chemistry of the Actinides*, 4, 413-455.

Kobashi, A., and G. R. Choppin, (1988) "A Study of Techniques for Separating Plutonium in Different Oxidation States," *Radiochim. Acta*, 43, 211-215.

Langmuir, D. (1997) *Aqueous Environmental Chemistry*, Prentice Hall, Upper Saddle River, New Jersey, p. 486-547.

Mahamid, I. A.; K. A. Becraft; H. Nitshce, (1995) "Complexation of plutonium (V) with nitrilotriacetic acid," *Radiochimica Acta*. 68, 63-68.

Mersman, K. E., (1982) "Special Wasteform Lysimeter Program Wasteform Characteristics." DPST-82-492, Westinghouse Savannah River Company, Aiken, SC.

McDowell-Boyer, L.; Yu, A. D.; Cook, J. R.; Kocher, D. C.; Wilhite, E. L.; Holmes-Burns, H.; Young, K. E., (2000) "Radiological Performance Assessment for the E-Area Low-Level Waste Facility," WSRC-RP-94-218, Westinghouse Savannah River Company, Aiken, SC.

Morgenstern, A.; G. R. Choppin, (2002) "Kinetics of the Oxidation of Pu(IV) by Manganese Dioxide," *Radiochim. Acta*, 90, 69-74.

Nelson, D.M., Larson, R.P., and Penrose, W.R., (1987) "Chemical Speciation of Plutonium in Natural Waters." In *Environmental Research on Actinide Elements*, J.E. Pinder, J.J. Alberts, K.W. McLeod, and R.G. Schreckhise (eds.), p. 27-48, CONF-841142, Office of Scientific and Technical Information, U.S. Department of Energy, Washington D.C.

Neumoev, N.V.; I. A. Korotkov; T. I. Semonva; A. A. Chizov; E. V. Renard, (1989) "Some characteristics of gas-chemical reduction of plutonium (VI) to plutonium (IV) by nitrogen-oxides in nitric-acid solutions," *Soviet Radiochemistry*. 31(2), 178-185

Nikitenko, S.I.; M.V. Nikonov; A.Y. Garnov, (1995) "Kinetics and kinetic isotope effect in pentavalent plutonium disproportionation activated by power unltrasound," *Journal of Radiological and Nuclear Chemistry*. 191, 361-267

Nikitenko, S.I.; N.N. Krot, (1989) "Kinetic isotope effect in the disproportionation reaction of pentavalent plutonium in the presence of di-(2-ethylherxyl)- phosphoric acid," *Doklady. Physical Chemistry*. 309: 965-968.

Nitsche, H., and Edelstein, N.M., "Solubilities and Speciation of Selected Transuranium Ions. A Comparison of a Non-Complexing Solution with a Groundwater from the Nevada Tuff Site" *Radiochim. Acta.*, 39, 23-33, 1985.

Oblath, S. B., (1984) "Defense Waste Lysimeters: 1983-84 Monitoring Report," DPST-84-859, E. I. du Pont De Neours and Company, Savannah River Laboratory, Aiken, SC

Orlandini, K. A.; W. R. Penrose; D. M. Nelson, (1985) "Pu (V) as the Stable Form of Oxidized Plutonium in Natural Waters," Mar. Chem., 18, 49-57.

Powell, B. A., R. A. Fjeld, J. T. Coates, D. I. Kaplan, and S. M. Serkiz. (2002) "Plutonium Oxidation State Geochemistry in the SRS Subsurface Environment," WSRC-TR-2003-00035, Rev. 0. Westinghouse Savannah River Company, Aiken, SC.

Rai, Dhanpat; R. J. Serne; J. L. Swanson, (1980) "Solution species of plutonium in the environment," *J. Env. Qual.*, V9, n3, 417-420.

Sanchez, A. L; T. Sibley; A. Murray, (1985) "The adsorption of plutonium IV and V on goethite," *Geochimica et Cosmochimica Acta*. 49, 2297-2307

Seaborg, G.T., and J. J. Katz, (1954) "*The Chemistry of the Actinide Elements*," John Wiley & Sons, Inc., New York.

Shilov, V.P., (1997) "Disproportionation of Plutonium (V) in Alkaline Media," *Radiochemistry*. 39, 328-331

Silva, R.J. and Nitsche, H. "Actinide Environmental Chemistry" *Radiochim. Acta.* 70/71, 377-396, 1995.

Sparks, D. L. (Editor) 1996. Methods of Soil Analysis, Part 3 – Chemical Methods. Soil Science Society of America Publishers, Madison, WI.

Sparks, D. L. 1996. Methods of Soil Analysis, Part 3 Chemical Methods. Soil Science Society of America, Inc, Madison, WI

Srivastava, R.D., (1988) *Heterogeneous Catalytic Science*. CRC Press. Boca Raton, Florida.

Stone, J. A.; S. B. Oblath; R. H. Hawkins; M. W. Grant; S. L. Hoeffner; C. M. King, (1985) "Waste Migration Studies at the Savannah River Plant Burial Ground," DP-MS-85-86, E. I. du Pont De Neours and Company, Savannah River Laboratory, Aiken, SC

Thomas, J.M.; W.J. Thomas, (1967) *Introduction to the Principles of Heterogeneous Catalysts*. Academic Press. London.

U.S. EPA (1991) 40 CFR Parts 141 and 142 – National Primary Drinking Water Regulations; Radionuclides; Proposed Rule. *Federal Register* 56, 33050.

APPENDIX A. DETAILED LABORATORY PROCEDURES

M&M Used to Remove Depth-Discrete Samples from the Mini-lysimeter Sediment M-6 Core: (Pu(OH)$_4$

7/30/02

1. Label on column: See lab notebook: wsrc-nb-2001-00133, page 85.
2. Tamped sediment in column from top.
3. Measured total length of soil column: 10.625 inches.
4. Cut column 5 inches from bottom.
5. Extruded sediment using ELE Intern. Sample Ejector in increments as shown in Appendix Table 1A.
6. Made second cut at 12 inches from bottom.
7. Extruded sediment in ½ and 1 inch sections.
8. Due to difficulties in measuring sample thickness correctly, primarily at bottom of column which had gone dry due to samplers neglecting to add core end cap, we had to adjust the thickness' of each sample to equal the total distance measured prior to collecting the depth discrete samples. The corrected sample thickness' are presented in column 5 of Appendix Table 1A.
9. Air dried and then thoroughly mixed sediment sample.
10. Submitted ~3-g air-dried sample to ADS for
    - Sodium-Peroxide Fusion Digestion and Nitric Acid Uptake
    - Pu-239 concentrations of total digestion

Appendix Table 1A. Actual sample collection order and depth.

ID #	Sample Collection Order	Tube Segment	Soil sample length (from bottom to top; inches)	Original label (inches)	Observations
201	1	1	0 to 2	0 to 1-7/8	± ¼ inch; very hard and dry; difficult to cut accurately
202	2	1	2 to 3	1-7/8 to 2-3/4	± ¼ inch, as above, very dry
203	3	1	3 to 3-5/8	2-3/4 to 3-5/8	± 1/8 inch, moist sample
204	4	1	3-5/8 to 4-1/8	3-5/8 to 4-1/8	± 1/8 inch,
205	5	1	4-1/8 to 4-5/8	4-1/8 to 4-5/8	± 1/8 inch,
206	6	1	4-5/8 to 5	4-3/8 to 5	± 1/8 inch, only ¼ inch sample; reassigned depth of all samples to account for this inconsistency
207	7	2	5 to 5-5/8	Same as col 4	± 1/8 inch, moist sample
208	8	2	5-5/8 to 6	Same as col 4	± 1/8 inch, moist sample
209	9	2	6 to 6-½	Same as col 4	± 1/8 inch, moist sample
210	10	2	6-½ to 7	Same as col 4	± 1/8 inch, moist sample
211	11	2	7 to 7-½	Same as col 4	± 1/8 inch, moist sample
212	12	2	7-½to 8	Same as col 4	± 1/8 inch, moist sample
213	13	2	8-½ to 9	Same as col 4	± 1/8 inch, moist sample
214	14	2	9 to 9-½	Same as col 4	± 1/8 inch, moist sample
215	15	2	9-½ to 10	Same as col 4	± 1/8 inch, moist sample
216	16	2	10 to 10-½	Same as col 4	± 1/8 inch, hole in middle of sample because of ¾ inch pebble, did not include pebble in sample; only pebble in column

M&M For Recovering Depth-Discrete Samples from the Mini-lysimeter Sediment M-7 Core

6/3/03

1. Conduct of Operations' R&D Hazards Screening Checklist is located in lab notebook: wsrc-nb-2001-00133, page 114.
2. Record all notes on column label into lab notebook.
3. Tamped sediment in column so that sediment is compacted at the bottom.
4. Measured total length of soil column is between 16.875 and 17.875 in (avg = 17.375 inches).
5. Cut column at ~7 and ~14 inches from bottom.
6. Extruded sediment using ELE International Sample Ejector in ½- and 1-inch sections in the order shown in Table 1.
7. Sample ID# 700, 14 – 17.375 inches from bottom, will be collected by digging out sediment from the 14 – 30 inch section of tube. We may attempt to further divide this section into 15 – 16 and 16 – 17.375 inches.
8. Place sediment in plastic weighing boats and then place the sediment-holding weighing boats in zip-locked bags.
9. Submitted ~3-g air-dried sample to ADS for
    - Sodium-Peroxide Fusion Digestion and Nitric Acid Uptake
    - Pu-239/Pu-238 concentrations of total digestion (Check with Dave Diprete)

Appendix Table 2A. Actual sample collection order and depth.

ID	Sample Collection Order	Tube Segment	Distance from Bottom, Slice Bottom	Distance from Bottom, Slice Top	Slice Thickness	Observation
		(in)	(in)	(in)	(in)	
700	6	0 to 6.5	0	1	1	moist
701	7	0 to 6.5	1	2	1	moist
702	8	0 to 6.5	2	3	1	moist
703	9	0 to 6.5	3	4	1	moist
704	10	0 to 6.5	4	4.5	0.5	moist
705	11	0 to 6.5	4.5	5	0.5	moist
706	12	0 to 6.5	5	5.5	0.5	moist
707	13	0 to 6.5	5.5	6	0.5	moist, slanted bottom due to non-square cutting of tube; bottom slice surface from 6 to 6.5 in. Sliced core to give flat surface.
708	14	6.5 to 9.875	6	6.5	0.5	
709	15	6.5 to 9.875	6.5	7	0.5	Filter located at 7 inches. Filter largely in tack and was in 1 piece. 2 or 3 pieces attached to soil that accounted for <3% of filter. Removed filter from soil sample.
710	16	6.5 to 9.875	7	7.5	0.5	Filter located at 7 in. See note above.
711	17	6.5 to 9.875	7.5	8	0.5	
712	18	6.5 to 9.875	8	8.5	0.5	
713	19	6.5 to 9.875	8.5	9	0.5	
714	20	6.5 to 9.875	9	9.5	0.5	
715	21	6.5 to 9.875	9.5	9.875	0.375	
716	22	6.5 to 9.875	9.875	10.875	1	
717	5	9.875 to 17.375	10.875	11.875	1	
718	4	9.875 to 17.375	11.875	12.875	1	
719	3	9.875 to 17.375	12.875	13.875	1	Dry. This sample totally crumbled & fell out of core. Slice top & bottom were estimated based on measurements from top & bottom of core. Contained 1 in rock; threw away.
720	2	9.875 to 17.375	13.875	16	2.125	Dry. Large portion of sample was not collected because it got contaminated with other sample.
721	1	9.875 to 17.375	16	16.625	0.625	
722	0.5	9.875 to 17.375	16.625	17.375	0.75	Dry. Top of core actually sloped from 16.25 to 17.75. After this slice was removed, the core was flat.
723			Filter**			Submit 1/4 the filter to ADS for analysis. Taken from 6.5 to 9.875 inches.
724			Background			Sediment from: "Control" M-11 Lysimeter

** **Filter**: The filter had a shape of a flattened circle with one dimension of 1 inch and a second dimension of 0.875 inches. The filter was cut in 4 equal parts. One section was submitted for total analysis. When the filter was cut, it broke apart, showing the 2 individual filters used to sandwich the $Pu(C_2H_4)_2$. An army green color circle could be seen in the middle of both filter papers; it form a circle with a diameter of ~1-cm (3/8 inch). This color is likely not the $Pu(C_2H_4)_2$, but instead is algae that fed on the C_2H_4. Pu(IV) is typically blue, whereas Pu(III) is green. Furthermore, you need ~0.1 Ci Pu-239 to see any color. The filter received only about 0.0005 Ci Pu-239.

M&M For Recovering Depth-Discrete Samples from the Mini-lysimeter Sediment M-9 Core

9/24/02

1. Label on column: See lab notebook: wsrc-nb-2001-00133.
2. Tamped sediment in column so that sediment is compacted at the bottom.
3. Measured total length of soil column: 15.625 inches.
4. Cut column 7 and 14 inches from bottom.
5. Extruded sediment using ELE International Sample Ejector in ½- and 1-inch sections in the order shown in Table 1. Sample ID# 220, 14 – 15.625 inches from bottom, will be collected by digging out sediment from the 14 – 30 inch section of tube.
6. Place sediment in plastic weighing boats and then place the sediment-holding weighing boats in zip-locked bags.
7. Submitted ~3-g air-dried sample to ADS for
    - Sodium-Peroxide Fusion Digestion and Nitric Acid Uptake
    - Pu-239/Pu-238 concentrations of total digestion (Check with Dave Diprete)

Appendix Table 3A. Actual sample collection order and depth.

ID #	Sample Collection Order	Tube Segment (inches)	Actual Soil Sample Depth (inches)	Target Sample Depth (from bottom, 0 inches, to top, 15.625 inches)	Observations
220	1	14 - 30		14 – 15.625	
221	2	0 - 7		0 – 1	
222	3	0 - 7		1 – 2	
223	4	0 - 7		2 – 3	
224	5	0 - 7		3 – 4	
225	6	0 - 7		4 – 4.5	
226	7	0 - 7		4.5 – 5	
227	8	0 - 7		5 – 5.5	
228	9	0 - 7		5.5 – 6	
229	10	0 - 7		6 – 6.5	
230	11	0 - 7		6.5 – 7	
231	12	7 - 14		7 – 7.5	
232	14	7 - 14		7.5 – 8	
233	15	7 - 14		8 – 8.5	
234	16	7 - 14		8.5 – 9	
235	17	7 - 14		9 – 9.5	
236	18	7 - 14		9.5 – 10	
237	20	7 - 14		10 – 10.5	
238	21	7 - 14		10.5 – 11	
239	22	7 - 14		11 – 12	
240	23	7 - 14		12 – 13	
241	24	7 - 14		13 – 14	

Materials and Methods for Geochemistry Processes Governing Plutonium Mobility Studies on M-9 Mini-Lysimeter $Pu(NO_3)_4$ Sediment Core

3/3/03

List of Experiments:

1. Pu(IV) Remobilization via Oxidation: Determine if sorbed Pu can be leached from the sediment under extreme, albeit unlikely, oxidizing conditions to promote Pu desorption.
2. SEM/EDX Analysis: Conduct SEM Backscattering analysis on clay particles collected from the core.
3. Groundwater Desorption Test: Determine desorption isotherm and desorption Kd values

Experiment 1: Pu(IV) Remobilization via Oxidation

Materials**:**

1. 1L SRS groundwater (TGH-1)
2. Sediment #228 – well mixed
3. 2 - 0.45μm disposable filtration systems

Methods:

1. Add 15g #228 sediment to each of two filtration systems, labeled "Rep 1" & "Rep 2".
2. Bubble air into 1L SRS groundwater using one or two frits. Keep this water constantly aerated. For first saturation, make sure water is aerated for >1hr.
3. Then follow Appendix Table 4A.
4. Label samples 261-1GW, 261-2GW, 262-1GW, 262-2GW.
5. Terminated experiment Tuesday April 15, 2003.
6. To save money, we will incrementally submit samples to ADS for $^{239/240}$Pu analysis. Submit only Rep 1 samples: 261-1GW, 262-1GW, 267-1GW, 273-1GW, & 279-1GW. We may submit more depending on the results from these tests. So prior to submitting to ADS, let me talk to Dave to request a quick turn-around-time.

Appendix Table 4A. Wet - dry cycling of sediment moisture

Day	Start of day	End of day
Monday	Add 25mL water. Cover.	
Tuesday	Remove cover. Suction Vacuum. Record sample volume. Add 0.36mL HNO_3. Stir sediment.	Stir.
Wednesday	Stir.	Stir
Thursday	Add another 25mL water. Cover.	
Friday	Remove cover. Suction Vacuum. Record sample volume. Add 0.36mL HNO_3. Stir sediment.	

Experiment 2: SEM/EDX Analysis

Materials:

1. Sediment #227 – well mixed
2. Sediment #223 – well mixed
3. 25g/0.5L Hexametaphosphate (HMP) Stock Solution
4. 10% HMP Solution: Bring 200mL HPM Stock Solution up to 2-L with water
5. 270-mesh (53µm) sieve

Methods:

1. Pass 15g of each sediment through the 270-mesh sieve. Wipe sieve very well with a slightly moist and then dry Kimwip between uses. Be sure to dry very well between uses.
2. Add 230mL of 10% HPM Solution to a 250-mL large-mouth Nalgene bottle. Transfer the <53µm clay/silt fraction into solution. Put on rotating shaker overnight.
3. Shake vigorously by hand for 1 minute. Mark top of water line and 5.9 cm below water line with a Sharpie. Loosen top and set in hood for 4.5 hours. Siphon suspension from the top 5.9 cm and save clay suspension. (I'll help you with this step.)
4. Bring volume back up to 230mL with 10% HMP Solution.
5. Repeat steps 2 & 3. Combine clay suspensions from the same sediment sample.
6. Save for Backscattering Analysis.

One Time Instructions for Preparing SEM/EDX Samples from Mini-Lysimeter M – 8, $PuO_2(NO_3)_2$

Dan Kaplan
2/26/03, Version 2.0

Submit the following samples to Wilson Smith in C-wing. Route the paperwork for the samples past Leigh Brown to get LIMS numbers. I have already talked with Wilson, so he knows what we are looking for.

For ADS forms, the total activity based on previous ADS $^{239/240}$Pu analyses on:
Stub P is ~2000 dpm (or ~20,000 dpm/g),
Stub Q is ~7 dpm (or ~70 dpm/g),
Stub R is ~1.5e6 dpm
Stub S is ~40,000 dpm (or ~4e7 dpm/g)

Stub P: <2-µm fraction of sediment 227. Set up disposable filtration system with a 0.45-µm filter placed on the existing filter. Shake vigorously the <2-µm fraction. Pipette ~5-mL onto filter paper, enough to cover the filter paper of the disposable system. Pull vacuum. Pull filter paper out of assembly. Air dry filtered clay. Expose sticky tape on stub and press sticky tape against dry clay. Objective: do EDX scans to determine if Pu is evenly spread over the particles or if the Pu exists as discrete particles, precipitates. This will help determine whether the Pu moved in association with colloids or not. The second objective of this sample is to determine whether the Pu is associated with areas that are high in Ti, Mn, Fe, Al, or Si.

Stub Q: <2-µm fraction of sediment 223. Same as for Stub P.

Stub R (2 samples on 1 stub): Filter paper and sediment. Place an aggregate of sediment & filter paper from sample #228 on stub. Try to make sample 2-dimentional. Objective: Conduct an EDX transect across the filter onto the sediment to see Pu mobility. Secondly, to see if Pu is associated with Ti, Mn, Fe, Al, or Si. Thirdly, to get semi-quantitative information about Pu concentrations on filter.

Filter paper opposite orientation from Stub R. Take a piece of the filter paper used in Stub R and orient it so that the opposite side of the paper is facing upward, i.e., the side that was against the soil aggregate is facing upward. Objective: To make sure Pu is not limited to existing solely on the opposite side of filter paper.

Stub S: Sediment #288: Mix sediment well. Stick dry sediment onto stub by pressing the stub with exposed sticky tape directly on sediment. Objective**:** See if Pu is evenly associated with fines and coarser particles. See if Pu concentrations covaries with Ti, Mn, Fe, Al, or Si.

Experiment 3: Groundwater Desorption Test

Materials

1. Sediments #223, #226, #227, #228, and #229 – well mixed
2. TGH-1 Groundwater

Method

1. Label centrifuge tubes 271Kd – 284Kd (See Appendix Table 5A). Add 2.0g air-dried sediment + 40mL TGH-1 Groundwater. In tube #283-Kd and #284-Kd only added 40-mL TGH-1 Groundwater.
2. Put on rotating shaker for 1 weeks.
3. Pass through a disposable 0.42µm polycarbonate filter.
4. Acidify to 2% HNO_3; add 740µL concentrated HNO_3 (this assumes a final sample volume of 37mL).
5. Submit acidified sample to Dave Diprete for Pu-239/240 analysis.

Appendix Table 5A. Sample description

Sample ID#	**Sediment**
271-Kd	#223
272-Kd	#223
273-Kd	#223
274-Kd	#226
275-Kd	#226
276-Kd	#226
277-Kd	#227
278-Kd	#227
279-Kd	#227
280-Kd	#229
281-Kd	#229
282-Kd	#229
283-Kd	No Soil
284-Kd	No Soil

APPENDIX B. MATERIALS AND METHODS, AND SEDIMENT ^{238}PU CONCENTRATION DATA FOR THE PU^{IV}(OH)$_4$ CORE

Appendix Table B1. Sediment ^{238}Pu concentrations the $Pu^{IV}(OH)_4$ core.

Sample middle (cm from bottom)	Total Pu-238 (dpm/g moist soil)	Total Pu-238 (pCi/g moist soil)
2.54	2.93E+03	1.32E+03
6.35	3.15E+06	1.42E+06
8.4201	6.99E+05	3.15E+05
9.84885	1.15E+05	5.18E+04
11.11885	1.22E+05	5.50E+04
12.2301	5.75E+04	2.59E+04
13.5001	6.68E+04	3.01E+04
14.7701	1.14E+05	5.14E+04
15.875	4.71E+06	2.12E+06
17.145	1.36E+05	6.13E+04
18.415	9.36E+05	4.22E+05
19.685	3.86E+04	1.74E+04
20.955	2.91E+04	1.31E+04
22.225	4.91E+03	2.21E+03
23.495	2.53E+04	1.14E+04

M&M Used to Remove Depth-Discrete Samples from the Mini-lysimeter Sediment M-6 Core: $(Pu(OH)_4$

7/30/02

1. Label on column: See lab notebook: wsrc-nb-2001-00133, page 85.
2. Tamped sediment in column from top.
3. Measured total length of soil column: 10.625 inches.
4. Cut column 5 inches from bottom.
5. Extruded sediment using ELE Intern. Sample Ejector in increments as shown in Appendix Table B2.
6. Made second cut at 12 inches from bottom.
7. Extruded sediment in ½ and 1 inch sections.
8. Due to difficulties in measuring sample thickness correctly, primarily at bottom of column which had gone dry due to samplers neglecting to add core end cap, we had to adjust the thickness' of each sample to equal the total distance measured prior to collecting the depth discrete samples. The corrected sample thickness' are presented in column 5 of Appendix Table B2.
9. Air dried and then thoroughly mixed sediment sample.
10. Submitted ~3-g air-dried sample to ADS for
    - Sodium-Peroxide Fusion Digestion and Nitric Acid Uptake
    - Pu-239 concentrations of total digestion

Appendix Table B2. Actual Sample Collection Order and Depth.

ID #	Sample Collection Order	Tube Segment	Soil sample length (from bottom to top; inches)	Original label (inches)	Observations
201	1	1	0 to 2	0 to 1-7/8	± ¼ inch; very hard and dry; difficult to cut accurately
202	2	1	2 to 3	1-7/8 to 2-3/4	± ¼ inch, as above, very dry
203	3	1	3 to 3-5/8	2-3/4 to 3-5/8	± 1/8 inch, moist sample
204	4	1	3-5/8 to 4-1/8	3-5/8 to 4-1/8	± 1/8 inch,
205	5	1	4-1/8 to 4-5/8	4-1/8 to 4-5/8	± 1/8 inch,
206	6	1	4-5/8 to 5	4-3/8 to 5	± 1/8 inch, only ¼ inch sample; reassigned depth of all samples to account for this inconsistency
207	7	2	5 to 5-5/8	Same as col 4	± 1/8 inch, moist sample
208	8	2	5-5/8 to 6	Same as col 4	± 1/8 inch, moist sample
209	9	2	6 to 6-½	Same as col 4	± 1/8 inch, moist sample
210	10	2	6-½ to 7	Same as col 4	± 1/8 inch, moist sample
211	11	2	7 to 7-½	Same as col 4	± 1/8 inch, moist sample
212	12	2	7-½to 8	Same as col 4	± 1/8 inch, moist sample
213	13	2	8-½ to 9	Same as col 4	± 1/8 inch, moist sample
214	14	2	9 to 9-½	Same as col 4	± 1/8 inch, moist sample
215	15	2	9-½ to 10	Same as col 4	± 1/8 inch, moist sample
216	16	2	10 to 10-½	Same as col 4	± 1/8 inch, hole in middle of sample because of ¾ inch pebble, did not include pebble in sample; only pebble in column

APPENDIX C. ADDITIONAL DATA

Appendix Table C1. Desorption Kd values measured from Pu(IV) lysimeter sediments

Our ID	Soil	Liquid Pu-239/240 (dpm/mL)	Liquid Pu-239/240 Error (%)	Avg Liq Pu-239/240 (dpm/mL)	Solid Pu-239/240 (dpm/g)	Kd Pu-239/240 (mL/g)	Avg Kd Pu-239/240 (mL/g)	%-Sorbed Pu-239/240 (%)	Avg % Sorbed Pu-239/240 (%)	Liquid Pu-238 (dpm/mL)	Liquid Pu-238	Solid Pu-238 (dpm/g)
271-Kd	#223	<8.23E-02	LLD	1.22E-01	6.55e2	>7959	4802	>0.9975	0.9961	<4.62E-02	LLD	1.51e1
272-Kd	#223	1.13E-01	66.62%		6.55e2	5796				<2.82E-02	LLD	1.51e1
273-Kd	#223	1.72E-01	42.17%		6.55e2	3808		0.9947		<6.00E-02	LLD	1.51e1
274-Kd	#226	7.70E-01	26.93%	8.37E-01	2.07e3	2688	2711	0.9926	0.9919	<4.90E-02	LLD	3.78e1
275-Kd	#226	1.18E+00	22.13%		2.07e3	1754		0.9886		<9.70E-02	LLD	3.78e1
276-Kd	#226	5.61E-01	20.43%		2.07e3	3690		0.9946		<1.29E-01	LLD	3.78e1
277-Kd	#227	5.24E+00	5.84%	4.90E+00	1.51e5	28817	31162	0.9993	0.9994	<8.55E-02	LLD	2.92e3
278-Kd	#227	4.18E+00	6.51%		1.51e5	36124		0.9994		5.76E-02	32.34%	2.92e3
279-Kd	#227	5.29E+00	5.02%		1.51e5	28544		0.9993		8.32E-02	26.71%	2.92e3
280-Kd	#229	1.45E+01	3.36%	1.10E+01	9.69e5	66828	92378	0.9997	0.9998	3.65E-01	13.50%	1.95e4
281-Kd	#229	9.72E+00	3.93%		9.69e5	99691		0.9998		1.84E-01	16.64%	1.95e4
282-Kd	#229	8.76E+00	5.70%		9.69e5	110616		0.9998		1.34E-01	29.58%	1.95e4
283-Kd	None	2.52E-01	LLD							<1.18E-01	LLD	
284-Kd	None	1.24E-01	LLD							<7.32E-02	LLD	