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Plutonium Oxidation State Transformations After 11 Years in Vadose Zone Sediments

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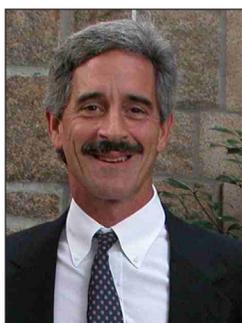
Pu mobility in the subsurface environment is largely controlled by its oxidation state; Pu(V) and Pu(VI) are typically two orders-of-magnitude more mobile than Pu(III) or Pu(IV). Micro-XRF studies revealed that Pu was very unevenly distributed on the sediment and Mn concentrations were too low (630 mg kg⁻¹) and perhaps of the wrong mineralogy to influence Pu distribution. Pu-XANES of the Pu(III) and Pu(IV)-amended lysimeters contained essentially identical Pu distributions, suggesting steady state had been achieved: 37% Pu(III), 67% Pu(IV), 0% Pu(V), and 0% Pu(VI). To our knowledge, this is the first observation of steady state Pu(III) in association with natural sediments.

Plutonium is an element of concern in disposal and remediation scenarios because of its radiotoxicity and very long half-lives for several isotopes. Once released into the environment, the movement of Pu is strongly related to its oxidation state. In aqueous solutions, Pu can exist in oxidation states III, IV, V, and VI, with two or three of these oxidation states commonly present at equilibrium. Pu(V) and Pu(VI) are typically two orders of magnitude more mobile than Pu(III) or Pu(IV).

A series of lysimeters were established on the Savannah River Site located in Aiken, South Carolina, to evaluate the long-term transport of Pu through vadose zone sediments. The vadose zone is the region below the root zone and above the underlying water table and is where radioactive waste in the U.S. is disposed. Five lysimeters were evaluated for this study: an unamended control and four lysimeters amended with Pu^{VI}O₂(NO₃)₂, Pu^{IV}(NO₃)₄, Pu^{IV}(C₂O₄)₂, or Pu^{III}Cl₃. The lysimeters consisted of inverted 52L bottomless carboys that were connected

to separate leachate collection reservoirs and filled with nearby vadose zone sediment. Pu-amended filter discs were buried and after being exposed to natural weather conditions for 11 years, the cores were collected containing the sediment and filter.

For the Pu(II)- and Pu(IV)-amended lysimeters, more than 95% of the Pu remained within 1.25 cm of the source after 11 years; the other 5% of Pu moved at an overall rate of 0.9 cm yr⁻¹. As expected, Pu moved more rapidly through the Pu(VI) lysimeter, at an overall rate of 12.5 cm yr⁻¹. The micro-x-ray fluorescence (micro-XRF) imaging of the sediment samples led to two key findings (**Figure 1**). First, Pu was not evenly dispersed throughout the samples. Instead, sediment Pu was rarely detected and when it was detected, it existed at high concentrations. Such a distribution is typical of (co)precipitated or colloidal phases. If the Pu were in fact individual Pu particles, these colloids would not be mobile because mobile colloids tend to be less than 1 μm, whereas those present in the μ-XRF were greater than 50 μm. The second general finding was that Pu concentrations did not correlate with Mn or Fe. Pu has been shown repeatedly to sorb strongly to Mn- and Fe-oxyhydroxides.



Authors (from left, top) Daniel Kaplan, Martine Duff, (bottom) Brian Powell, and Miles Denham

Figure 2 presents examples of sediment and standard mi-

croprobe Pu-X-ray Absorption Near Edge Spectroscopy (XANES) spectra at the Pu L₃ absorption edge. Calibration error estimates on these values are about 25%. The average oxidation state of Pu in the Pu^{III}Cl₃ and Pu^{IV}(NO₃)₄ filter discs indicate that the Pu oxidation states had changed since being placed in the

ground (**Table 1**). In both cases, no Pu(V) or Pu(VI) was detected and varying fractions of Pu(III) and Pu(IV) are present. The proportion of Pu(III) and Pu(IV) measured in the samples appear to have been influenced by the original oxidation state of the material. This suggests that the two source materials may

not have yet reached steady state. Pu(III) is rarely, if ever, reported in natural sediments exposed to air. Based on thermodynamic considerations, Pu(III) may have a wide natural occurrence especially in acidic environments and therefore its existence may warrant further investigation.

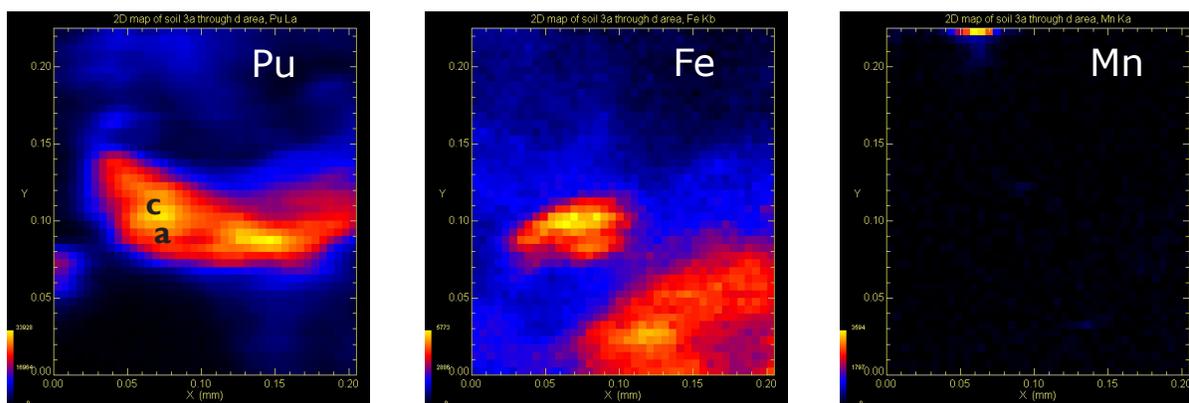


Figure 1. Micro-SXRF elemental map images of sediment next to the: Pu^{IV}(NO₃)₄- amended filter disc. Regions "a" and "c" identify the locations where the Pu-XANES spectrum presented in Figure 2 were collected. Relative concentrations on these maps increase from black (least concentrated), blue, red, and yellow (most concentrated). Data collected at X-ray beamline X26A.

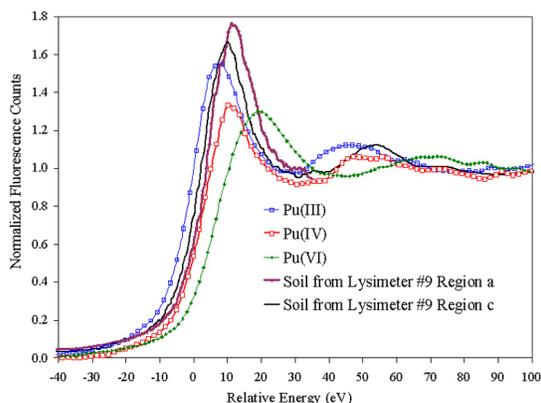


Figure 2. The Pu-XANES spectra for the standards [Pu(IV) and (VI)] and regions "c" and "a" on the sediment taken next to the Pu(IV)-spiked filter in the Pu(NO₃)₄-amended lysimeter (Lysimeter #9; see Figure 1). The spectra demonstrate the edge energy shift with oxidation state at the half height of the edge step (i.e., when Normalized Fluorescence Counts = 0.5). The average edge energy for sediment from Pu(NO₃)₄-amended lysimeter (region "c") is roughly midway between Pu(III) and Pu(IV) which, based on relative edge energy, would be consistent with a mixed Pu(III/IV) species. Data collected at X-ray beamline X26A.

Lysimeter Sample	Pu(III) ± Stdev ^(a) (%)	Pu(IV) ± Stdev ^(a) (%)	Number of XANES Measurements
Pu(NO ₃) ₄ filter disc	21 ± 17	77 ± 17	7
PuCl ₃ filter disc	52 ± 3	48 ± 3	3
Sediment in contact with Pu(NO ₃) ₄ filter disc ^(b)	38 ± 18	63 ± 18	10
Sediment in contact with PuCl ₃ filter disc ^(b)	35 ± 17	65 ± 17	7

^(a) Only Pu(III) and Pu(IV) species were assumed to be present for these calculations.
^(b) Sediment was separated from the filter disc prior to XANES measurement.

Table 1. The calculated average distribution for Pu(III) and Pu(IV) in the lysimeter samples based on edge energy in comparison to spectra for Pu(IV) in PuO₂(s) and Pu(III) in PuBr₃(s).