Biogeochemistry of the Pond B Water Column, Savannah River Site, South Carolina

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Pond B at Savannah River Site (SRS) is an ideal location for examining the biogeochemical cycling of Fe, Pu, organic matter, and other metals in a monomictic stratified pond. This pond received reactor cooling water from 1957–1964 containing trace levels of radionuclides. Since then, Pond B has remained relatively isolated except for a few studies conducted in the late 1980s, which demonstrated Pu cycling with seasonal anoxia.
During summer thermal stratification, aqueous concentrations of Pu, Fe and ^{137}Cs increase with depth coupled with anoxia, low Eh, and high suspended solids, likely linked to reductive dissolution of Fe-(oxy)hydroxides and mobilization of organic matter. These trends are consistent with 1983 measurements of ^{239,240}Pu and ^{137}Cs activities in Pond B, although Pu and decay-corrected ^{137}Cs activities have since decreased 2- to 3-fold in the water column. Pu isotopic ratios in water samples are consistent among all locations and depths and are similar to ratios of upstream sediments, suggesting that Pu in the pond is dominantly from historical releases and not atmospheric fallout.
The microbial community was also examined to understand biotic mechanisms that impact Pu and Fe cycling. We observed that during stratification, the Pond B water column microbiome varies with depth rather than spatial location and can be broadly categorized by the three distinct stratification layers. Metal (e.g., iron) oxidizers/reducers were prevalent during stratification, likely influencing Pu immobilization onto Fe-(oxy)hydroxides in the thermocline and Pu mobility/reduction in the deep, anoxic layer. Notably, Fe(II) oxidizers were most abundant in the hypoxic/anoxic zones, while Fe(III) reducers dominated the deep, anoxic layer. In contrast to summer stratification, during spring turnover, the microbiome is homogenized throughout Pond B, reflecting the uniform geochemistry (e.g., oxygen concentrations, temperature, metals).
We also observed a shift in the distribution and abundance of organic molecules (dissolved organic matter; DOM) with depth and location. Multivariate analysis based on bulk molecular parameters and relative abundance of individual elemental formulas showed that the molecular composition of DOM was highly stratified and could be separated into three distinct layers in the summer. Surface layer samples were characterized by higher nominal oxidation state of carbon, H/C, and aliphatic compounds. In contrast, the deep anoxic zone was characterized by higher DBE (double bond equivalent), DBE/O, aromatic index, and CRAM (carboxyl rich alicyclic molecules), indicating that the DOM in the deep layer was more refractory.

Factors Controlling Pu-239 and Cs-137 Mobility in Contaminated Isolated Pond Sediments, Savannah River Site, South Carolina

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There remains a lack of knowledge regarding ecosystem transfer, transport processes, and mechanisms, which influence the *long-term* mobility of ^{239}Pu and ^{137}Cs in natural environments, particularly with respect to how anthropogenic radionuclides interact with natural biogeochemical cycles. Furthermore, monitoring the distribution and migration of trace anthropogenic radioisotopes as ecosystem tracers has the potential to provide insight into the underlying mechanisms of geochemical cycles. This study investigated the distribution of the anthropogenic radionuclides ^{239}Pu and ^{137}Cs, along with total organic carbon, iron and trace element concentrations, and the microbial community in contaminated sediments of Pond B at the Savannah River Site (SRS) in South Carolina.
Pond B received SRS R-reactor cooling water from 1957–1964, resulting in trace amounts of ^{239}Pu and ^{137}Cs being introduced into the pond. Since then, the pond has been relatively isolated except for a sampling campaign in the 1980s evaluating radionuclide distributions in the water and sediment. In this work, sediments were collected throughout the Pond B site to determine the spatial variability of Pu and Cs, as well as sediment cores to determine the concentrations of 239Pu, 137Cs, and major and minor elements in the solid phase. Additionally, an electrochemical method using an in-situ core probe was used on wet cores before extraction to determine the concentration and speciation of dissolved redox-active species.
More than 50 years after deposition, ^{239}Pu and ^{137}Cs concentrations in Pond B sediments are primarily located in the upper 5 cm of sediment in an area where deposition of particulate-bound contaminants was most prevalent and located between 5 and 10 cm in areas of high sedimentation. An analysis of the geochemical data coupled with a factor analysis demonstrated different sediment facies across the pond which result in a range of geochemical processes controlling the accumulation of Pu and Cs in the sediment. The highest concentrations of ^{239}Pu and ^{137}Cs appear to be controlled by particulate input from the influent canal. Elevated ^{239}Pu concentrations in the sediments were observed in areas with high organic matter content and high sedimentation rates indicating strong association of Pu with organic matter. Notably, the sediment microbial community at the pond outlet is likely involved in organic matter degradation processes and may impact Pu-associated organic matter.

Plutonium Distribution among Acidic Processing Waste at the Hanford Site, USA: Implications to Long-Term Subsurface Migration

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Between 1955 and 1962, 4 million liters of plutonium (Pu) reprocessing waste from the Plutonium Finishing Plant at the Hanford Site, containing an estimated 50-140 kg Pu, were pumped into the sediments of the 216-Z-9 (Z-9) trench. The waste consisted of high salt (~ 5M NO_3^-, ~ 0.6M Al^{3+}), acidic (pH ~ 2.5) solutions, that also contained the organic solvents: CCl_4, TBP, DBBP, and lard oil. While most of the Pu was observed to precipitate within the first several centimeters,[1] a small fraction of Pu has been detected in the vadose zone at depths of 37 m.[2] The mechanisms controlling Pu migration beneath the trench are unknown. In this study, a series of binary and ternary batch experiments were used to determine Pu partitioning behavior between aqueous, organic, and solid phases representative of the waste constituents and natural sediments of the Z-9 trench. The Pu partitioning behavior observed in the binary and ternary experiments was then used to develop a conceptual model for the transport of Pu in the subsurface.
Our results show that Pu can migrate as a Pu-TBP-nitrate complex in the presence of a TBP-containing organic phase under low pH and high nitrate conditions. Reducing the nitrate concentrations or increasing the pH will lead to Pu partitioning into the aqueous phase and subsequent sorption to native Hanford sediments. Our findings suggest that Pu migration in the subsurface is likely controlled by weak sorption of aqueous Pu under acidic conditions as well as with the formation of Pu-TBP-nitrate complexes in the organic phase. Dispersion of the nitrate plume and the transient nature of the low pH conditions will limit long-term Pu mobility beneath the trench.

1. Ames, L. L. Characterization of Actinide bearing soils: Top sixty centimeters of 216-Z-9 enclosed trench; Richland, WA, **1974**.
2. Cantrell, K. J.; Riley, R. G. A review of subsurface behavior of plutonium and americium at the 200-PW-1/3/6 operable units; **2008**.