Biogeochemical Cycling and Environmental Stability of Pu Relevant to Long-Term Stewardship of DOE Sites

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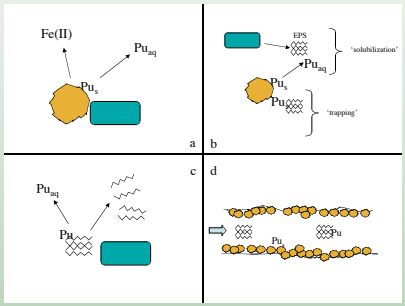
The overall objective of this research is to understand the biogeochemical cycling of Pu in environments of interest to long-term DOE stewardship issues. Central to Pu cycling (transport initiation and immobilization) is the role of microorganisms. The hypothesis underlying this work is that microbial activity is the causative agent in initiating the mobilization of Pu in near-surface environments: through the transformation of Pu associated with solid phases, production of extracellular polymeric substances (EPS) carrier phases and the creation of microenvironments. Also, microbial processes are central to the immobilization of Pu species, through the metabolism of organically complexed Pu species and Pu associated with extracellular carrier phases and the creation of environments favorable for Pu transport retardation.



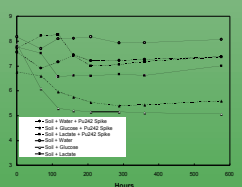
Schematic summary of the primary biogeochemical processes that are being investigated in this work: a) The release of sorbed Pu through either direct or indirect microbial action (rectangle) through the destruction of the host phase (irregular disk); b) 'Scavenging' of Pu from the immobile phase by microbially-produced ligands. Alternatively, the ligands, by sorbing onto the immobile phase, may 'trap' Pu by blocking desorption; c) Biodegradation of Pu / organic ligand complexes; d) Mobilization of Pu under advective flow conditions by microbially-generated EPS.

Effect of Microbial Processes on Pu Mobilization in Contaminated Soil

Materials and Methods: Soil Incubations

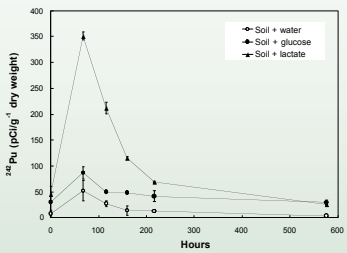
- 5 g RFETS 903 pad 'lip' soil (250 pCi ^{239}Pu g^{-1})
- 75 ml 0.5% glucose or lactate, and 0.015% NH_4Cl
- Anaerobic (N_2), 22 ± 2°C, unshaken
- Select samples spiked with tracer:40 nCi ^{242}Pu ($5x10^{-7}$ M or 8 nCi g^{-1} dry weight)
- Periodically determine pH, total gas, aqueous metabolites, Fe, and ^{242}Pu before and after filtration (0.45µm) by LSC; ^{239,240}Pu by α-spec.

Soil from the 903 pad 'lip' at the Rocky Flats Environmental Technology Site (RFETS) incubated with deionized water, glucose (middle) and lactate (right). The ^{239,240}Pu in this soil is predominantly associated with the inert fraction as well as iron oxides.

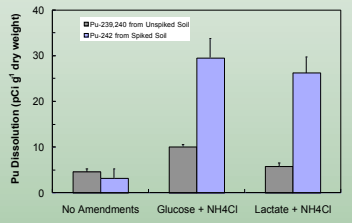


At 3 days incubation the pH of glucose amended soils decreased to 5.4; in lactate amended samples it increased to 8.3 in spiked treatments.

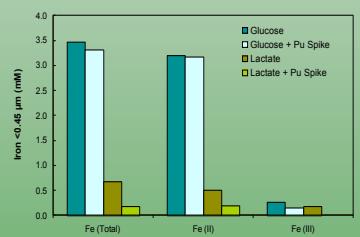
Dissolution of ^{242}Pu (<0.45µm) in 'Spiked' RFETS Soil Incubation



The concentration of ^{242}Pu in the filtrate (<0.45 µm) of amended samples increased due to microbial activity and remained at ~30 pCi g^{-1} dry wt.

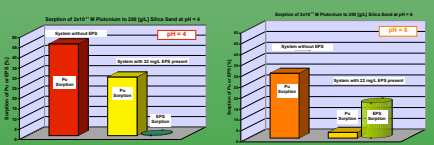


At the end of the incubation period (30-45 days), the greatest amount of Pu was detected in the solution phase of glucose-amended soil.



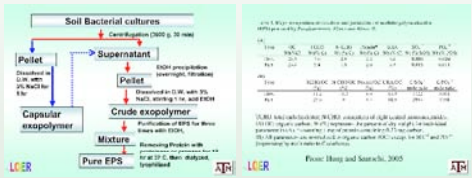
Iron reduction and dissolution occurred to the greatest extent in glucose-amended samples.

Effect of EPS on the sorpton of Pu to a quartz sand (pH$_{pzc}$ = 6.2).



Sorption of 10^{-11} M of ^{241}Pu to 200 [g/L] silica sand at pH = 4 and pH = 6, in the presence and absence of *Pseudomonas fluorescens* EPS (22 mg/L EPS, I = 0.001 M NaCl). The presence of EPS decreases Pu sorption at both pH values. However, the extent of the sorption decrease and the sorption behavior of EPS is a function of pH.

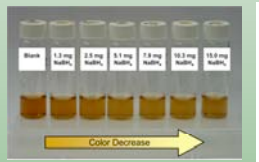
Characterization of Bacterial EPS

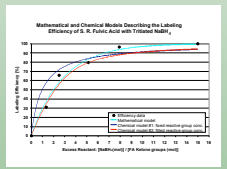


The neutral monosaccharides in this EPS consist of rhamnose, fucose, ribose, arabinose, xylose, mannose, galactose and glucose. The acidic groups in this EPS are mainly composed of carboxylic acid and minor polyanionic groups, e.g., sulfate and phosphate. Up to 70 % of total carbohydrates are uronic acids, and total carbohydrates made up 26-31% of organic carbon. Besides the neutral and acidic sugars in the EPS, EPS also contained 2% of proteins in terms of carbon, which makes the EPS amphiphatic (amphiphilic).

Analytical methods development: labeling NOM, EPS with ^{3}H

Observing the behavior of Pu / EPS complexes at environmentally-relevant concentrations requires a means of monitoring EPS below the limit of traditional OC analytical procedures. Below is a summary of a new method for radiolabeling NOM with ^{3}H.





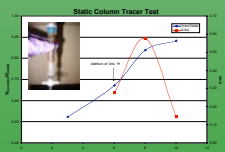
Based on the proposed labeling method, reactive groups of Suwannee River fulvic acid (FA) are reduced with tritiated sodium borohydride ($NaBH_4$) to label FA with tritium. FA is being used to test the procedure because of limited EPS quantities.

In this experiment, the reduction efficiency is determined for this reaction, which involves aromatic and aliphatic ketones as well as quinone groups of FA. For this purpose, various concentrations of $NaBH_4$ (0 – 15 mg) were added to solutions with equal concentrations of FA (10 mg) and the reaction mixture was stirred at an elevated temperature in an anaerobic environment.

At the end of the reaction time, each sample was scanned on a UV/VIS spectrometer for comparison with a FA blank containing no $NaBH_4$. The reduction of FA-carbonyl groups to secondary alcohols with sodium borohydride results in a color reduction of FA, which is assumed to be linearly proportional to the number of FA-reactive groups reduced.

'Static columns' for assessing Pu mobility under variable chemical, microbiological conditions.

Incubated 'static' columns are being utilized to examine the microbially-stimulated 'solubilization' of Pu. An advantage of static columns over more traditional batch experiments is the that they allow the assessment of the potential for Pu transport at solid/solution ratios appropriate for saturated groundwater systems without the complexity of full column studies.



Assessment of soil flushing efficiency prior to column incubation experiments. Fractional recovery of ^{3}H as a function of added volume for 5 g of Rocky Flats soil. A_o is the initial ^{3}H activity.

- Anaerobic microbial activity in RFETS soils resulted in dissolution of ^{242}Pu and ^{239,240}Pu in conjunction with iron-reduction.
- The identity of Pu is most likely a colloidal species in association with iron and an organic phase and is currently being investigated.

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