Lawrence Livermore National Laboratory

LLNL SFA OBER–SBR FY19 Program Management and Performance Report:

BioGeoChemistry of Actinides

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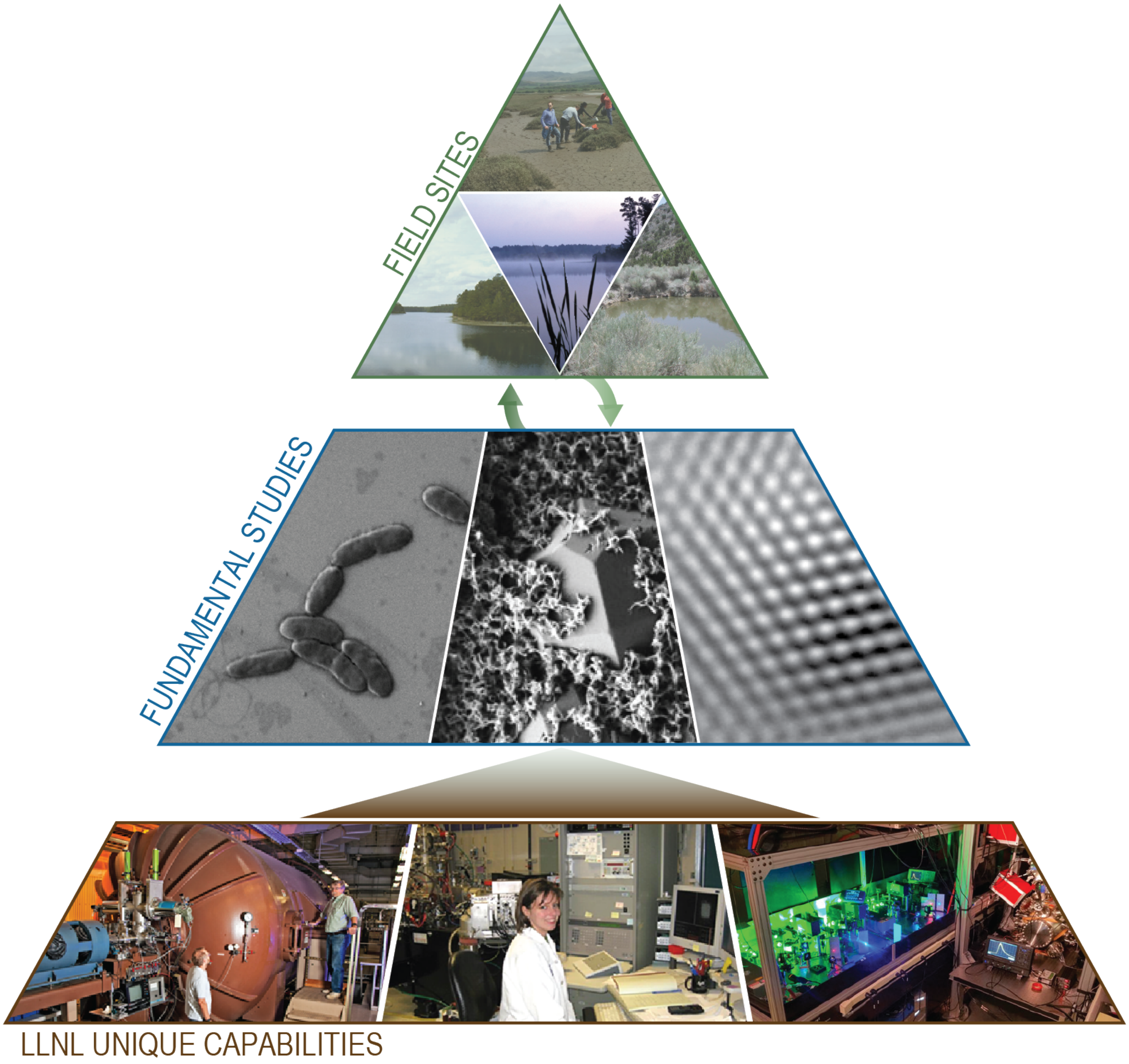

Integration of three core elements in the BioGeoChemistry of Actinides Scientific Focus Area.

1. PROGRAM OVERVIEW

BioGeoChemistry of Actinides

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Over 2,600 metric tons of plutonium (Pu) are estimated to have been produced worldwide, with approximately 70-90 metric tons added to this inventory each year from spent nuclear fuel. A subset of this Pu inventory has been released into the environment as a result of nuclear weapons production, weapons testing, poor waste management practices, and nuclear accidents. The migration of low levels of Pu released in the environment has been documented on the scale of kilometers. Due to its long half-life, toxicity, and its ability to migrate, Pu represents a potentially significant risk to humankind and the environment. Their fate depends on the nature of the release, the biogeochemical processes controlling mobilization, and the eventual exposure pathways. Understanding their behavior in the environment is critical for managing environmental contamination and planning for the safe, long-term isolation of nuclear waste from the biosphere.

The focus of the BioGeoChemistry of Actinides SFA is to identify and quantify the biogeochemical processes and the underlying mechanisms that control actinide mobility in an effort to reliably predict and control the cycling and migration of actinides in the environment. The research approach includes: (1) Field Studies (Research Thrust 1) that capture actinide behavior on the timescale of decades and (2) Fundamental Laboratory Studies (Research Thrust 2) that isolate specific biogeochemical processes observed in the field (cover art figure). These Research Thrusts are underpinned by the unique capabilities and staff expertise at Lawrence Livermore National Laboratory, allowing the *BioGeoChemistry of Actinides SFA* to advance our understanding of actinide migration behavior in the environment, and serve as an international resource for environmental radiochemistry research. Research Thrusts 1 and 2 are guided by broad central hypotheses:

Thrust 1 Hypothesis: *Biogeochemical processes occurring on the timescale of years to decades lead to greater actinide recalcitrance in sediments and limits their migration in surface and groundwater.*

Thrust 2 Hypothesis: *Long-term biogeochemical processes include mineral and surface alteration, which leads to stabilization of actinide surface associations or incorporation into mineral precipitates.*

Our strategic goal is to use the knowledge gained from this Science Plan to advance our understanding of the behavior of actinides, providing DOE with the scientific basis for remediation and long-term stewardship of DOE's legacy sites and, more broadly, increasing our understanding of transport phenomena in environmental systems sciences with a particular emphasis on environmentally relevant (long-term) timescales.

2. SCIENTIFIC OBJECTIVES

The goal of LLNL's SFA is to identify and quantify the biogeochemical processes that control the fate and transport of actinides in the environment. In FY19, our focus continues to be on Pu and directly supports the research goals of the Subsurface BioGeoChemical Research (SBR) program within BER to:

- Quantify how biological behavior, abiotic-biotic interactions, and molecular transformation control the mobility of contaminants and critical elements
- Translate biogeochemical behavior across relevant molecular to watershed scales to accurately and tractably predict flow of water, nutrients, and contaminants
- Quantify and predict how hydrologic systems drive biogeochemical processes in *contaminated* surface-subsurface systems.

Key Research Gaps

- Factors affecting long-term stabilization of actinides in sediments
- Actinide incorporation into secondary mineral phases in sediments
- Actinide stabilization on surfaces when coupled to redox cycles
- The role of microbes and their exudates in actinide mobilization and stabilization in sediments

We have identified the following key objectives of our Science Plan that are centered on a theme of processes and mechanisms that may affect the long-term behavior of actinides in the environment:

- Characterize the migration behavior of actinides across a wide range of hydrologic regimes (vadose zone, pond, estuary), a wide range of actinide concentrations, and environmentally relevant timescales (decades)
- Quantify actinide incorporation into iron oxides, carbonates, and aluminum oxides as a mechanism that may contribute to long-term actinide stabilization in sediments
- Determine the role of Fe(II)/Fe(III) cycling in stabilizing actinides as adsorbed species and/or surface precipitates on iron oxide and clay minerals
- Evaluate the role of microbes and their cell exudates in the mobilization of Pu and formation of ternary complexes on mineral surfaces.

3. PROGRAM STRUCTURE

Dr. Henry Shaw is the Laboratory Research Manager of LLNL's OBER programs. He is the Deputy Associate Director for S&T in the Physical and Life Sciences directorate (PLS) and reports directly to the Associate Director of PLS, Dr. Glenn Fox. Dr. Mavrik Zavarin is the Director of the Glenn T. Seaborg Institute (Seaborg Institute) housed in PLS and reports directly to Glenn Fox. This SFA program is aligned with the Seaborg Institute's research focus on environmental radiochemistry and education (*https://seaborg.llnl.gov*). Dr. Kersting is the Technical Co-Manager and oversees, together with Dr. Zavarin, this SFA's scientific program. Dr. Zavarin and Dr. Kersting provide scientific leadership to this SFA and communicate BER's program needs to the Focus Area Management Team (Figure 1). They co-mentor their postdocs and communicate two to three times a week to discuss laboratory safety, program management, experiment schedules, research results, and deliverables. Off-site collaborators participate in the bi-weekly meeting through web conferencing. The SFA Team meets weekly to present updates, discuss safety to review SFA research accomplishments, goals, and program plans.

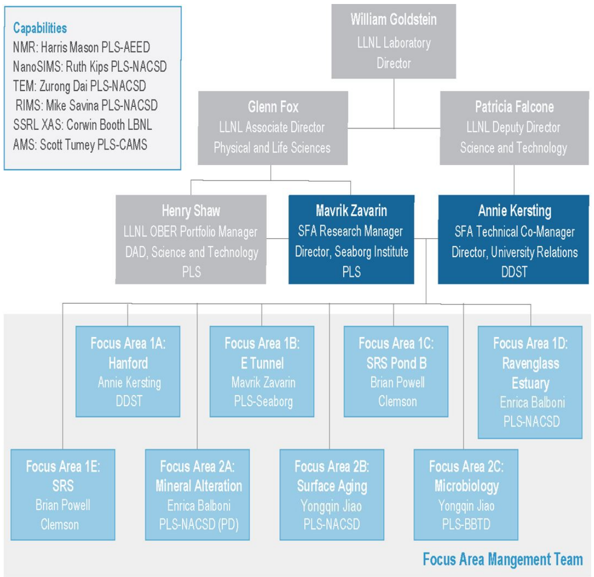


Figure 1. BioGeoChemistry of Actinides SFA management organization chart.

Data Management Plan

We are committed to the open sharing of LLNL SFA documentation and data in any form that is suitable for BER's data management plans. To facilitate best practices, Dr. Kersting serves on the new Environmental System Science Data Infrastructure for a Virtual Ecosystem (ESS- DIVE, *https://data.ess-dive.lbl.gov/*) Archive Committee along with postdoc, Nancy Merino. We are part of ESS-DIVE's pilot program to develop an inter-operable system for standardizing metadata and sample identifiers, enabling data processing and analysis that enhances the model-experimental (MODEX) approach. During our preparations for field sampling at SRS Pond B (Focus Area 1D), we have extensively discussed metadata collection and sample tracking with the ESS-DIVE committee and have incorporated the committee's chosen sample identifiers, known as the International Geo Sample Numbers (IGSN), into our field campaign. The metadata collected at SRS Pond B, including geochemical and microbial analyses, will be uploaded to ESS-DIVE and linked to our upcoming peer-reviewed publications. In addition, these data will be made publicly available within two years.

Education and Outreach

We have a strong educational component in our SFA, as we believe that training postdocs and graduate students provides a pipeline of talent to our SFA, the national laboratories, and the broader scientific community. Our educational efforts have enhanced the scientific productivity of this program, built a strong collaborative national and international research community, and leveraged our SFA funding. We have research collaborations with seven national and international research groups. Currently, this SFA supports 4 LLNL postdocs (Previous postdocs, Dr. Keith Morrison and Dr. Enrica Balboni, were recently converted to staff scientists). In addition, our subcontract supports a postdoc at Lawrence Berkeley National Laboratory (LBNL) and one at Clemson University.

To strengthen and expand our university collaborations, we have leveraged the Seaborg Institute's longstanding Student Internship Program. Each year about eight to ten students spend the summer at LLNL carrying out research in the areas of nuclear forensics and environmental radiochemistry. The Seaborg Institute also participates in the DOE-EM radiochemistry traineeship program at Washington State University, providing funding for two graduate students to perform research at LLNL. In 2018, we had four students work directly on our SFA, resulting in research conducted as part of their PhD. One student (Mitchell Friend) is now a post-doc at Los Alamos National Laboratory (LANL). A second student (Corey Pilgrim) is currently a DOE-NE postdoctoral fellow at Idaho National Laboratory (INL). Nate Conroy was a graduate student working on this SFA at Clemson University and is now a post-doc at LANL.

Personnel

Mavrik Zavarin—Director of the Glenn T. Seaborg Institute; a soil scientist involved in experimental and modeling studies of radionuclides at the mineral-water interface, mineral dissolution/precipitation kinetics, colloid-facilitated transport, and radionuclide reactive transport modeling. Dr. Zavarin is the Program Manager on this SFA and is responsible for overall planning and execution of the research program. Along with Dr. Kersting and Dr. Jiao, he co-mentors and directs the research for all the postdocs and graduate students. Together with Dr. Kersting, he is responsible for building and maintaining external collaborations. He leads Thrust 1 and engages with all Focus Areas.

Annie Kersting— Director of University Relations & Science Education at LLNL; a geochemist with expertise in isotope geochemistry, actinide chemistry, colloid-facilitated transport, and field investigations of contaminant transport. She is the technical co-manager for this SFA, and she helps drive the research agenda with Dr. Zavarin. Together with Dr. Zavarin, she co-mentors all the SFA postdocs and graduate students. She leads Thrust 2 and engages with all Focus Areas.

Yongqin Jiao—LLNL Group Leader of Systems & Synthetic Biology; a geobiologist who conducts research in environmental microbiology and biogeochemistry. Her research focuses on microbe-metal interactions, exploring metabolic activities of microbes and microbial communities concerning geochemistry and biotechnology of metals. Dr. Jiao co-mentors postdocs Nancy Merino and Chao Pan. She leads Thrust 2 Focus Area 2C: Microbial influences on actinide stabilization and mobilization and Focus Area 2B: Surface aging.

Brian Powell—Field Professor, Clemson University, Dept. of Environmental Engineering & Earth Sciences and Dept. of Chemistry; Dr. Powell's research focuses on understanding and quantifying the rates and mechanisms of actinide interactions with natural soils and synthetic minerals. He leads Thrust 1 Focus Areas 1D: Savannah River Pond B and 1E: RadFlex facility.

Corwin Booth—LBNL staff scientist; a physicist with expertise in strongly correlated f-electron systems and an expert in applying EXAFS theory. He is leading XAS data collection and analysis efforts and mentors postdoc Kurt Smith.

Harris Mason—LLNL staff scientist and Director of the Magnetic Resonance center at LLNL. Dr. Mason's research focuses on developing advanced solution and solid-state NMR spectroscopic methods to investigate metal sorption reactions at mineral-water interfaces. He is the lead for NMR capabilities.

Scott Tumey—LLNL staff scientist; an expert in accelerator mass spectrometry. He is the lead for AMS capabilities.

Keith Morrison—LLNL staff scientist; a biogeochemist with expertise in organic chemistry, biochemistry, microbiology and geology. He is investigating actinide behavior in the presence of microbes, minerals, and NOM.

Enrica Balboni—LLNL staff scientist; a radiochemist with expertise in actinide chemistry, mineralogy, isotope geochemistry, and mineral synthesis. Dr. Balboni has been studying Np and Pu substitution in sulfate and carbonate mineral phases, and adsorption to mineral surfaces. She leads Thrust 1 Focus Area 1A: Ravenglass and Thrust 2 Focus Area 2A: Actinide incorporation into mineral precipitates.

Chao Pan—LLNL postdoctoral fellow (started March, 2018). Dr. Pan has a background in aquatic chemistry and environmental geochemistry. She has studied the redox interaction between chromium, iron, and manganese at the solid-water interface. She recently received her PhD from Washington University, St. Louis. Dr. Pan is studying the behavior of Pu during Fe(II)/Fe(III) redox cycling and the role of NOM.

Stefan Hellebrandt—LLNL postdoctoral fellow (started April, 2018). Dr. Hellebrandt has a background in geology and radiochemistry. He has been applying synchrotron technique to study actinide interaction with mica surfaces. He received his PhD from the Helmholtz Zentrum Dresden Rossendorf, Germany. Dr. Hellebrandt is studying the transport processes controlling Pu migration at the Hanford site.

Nancy Merino—LLNL postdoctoral fellow (started January, 2019). Dr. Merino is a microbiologist with expertise in environmental microbiology, microbe-metal interactions, and bioinformatics. She has broad experience with bioremediation, metagenomics, and single-cell genomics. She received her PhD at UCLA and completed postdoctoral studies at the Earth-Life Science Institute (Tokyo Institute of Technology) and the University of Southern California. Dr. Merino is studying microbial ecology at the SRS Pond B.

Gauthier Deblonde—LLNL postdoctoral fellow (started April, 2019). Dr. Deblonde is a radiochemist with expertise in actinide science, hydrometallurgical processes, ligand-metal interactions, and speciation studies. He has previously completed a postdoctoral fellowship at LBNL within the DOE heavy element chemistry program. Dr. Deblonde is studying the interaction of Pu and other actinides with NOM actinide chelators.

Kathryn Peruski – Graduate student, Clemson University, Environmental Engineering and Earth Sciences; Ms. Peruski is involved in the RadFlex experiments and assisting in field sampling and soil characterization at the SRS Pond B.

4. PERFORMANCE MILESTONES AND METRICS

The Table 1 Timeline shows the planned schedule for each task (as adjusted in the program revision letter dated November 16, 2018) and makes note of any adjustment to the schedule made since that time. Importantly, as part of this program revision, our effort at the Hanford site was reduced such that it will be completed at the start of FY21. The effort at the SRS Pond B was moved up by almost a full year. To expedite this effort, we hired a new postdoc (Nancy Merino), performed a field reconnaissance in late January, 2019, and are performing our first full-field sampling exercise in late June 2019. Lastly, we reduced the scope associated with the formation of actinide-Al solution complexes task to reflect a reduced emphasis on the Hanford site in year 3 of the program.

Table 1. Timeline for each task identified in this Science Plan. Green: removed from schedule, purple: added to schedule.

	Focus Area and Task	**FY19**				**FY20**				**FY21**			
THRUST 1: FIELD STUDIES - BIOGEOCHEMICAL PROCESSES AFFECTING ACTINIDE TRANSPORT IN THE ENVIRONMENT	Focus Area 1A: Hanford Z-9 vadose zone actinide migration												
	Task 1A-1: Pu complexation with reprocessing waste	🟦	🟦	🟦	🟦*								
	Task 1A-2: Reactions between sediments and Pu reprocessing waste	🟦	🟦	🟦	🟦	🟦	🟦*						
	Task 1A-3 Pu reprocessing waste reactive transport through sediments			🟦	🟦	🟦	🟦	🟦	🟦	🟦*			
	Focus Area 1B: Ravenglass/Sellafield radionuclide migration in estuary sediments												
	Task 1B-1: Characterization of Ravenglass estuary actinide profiles	🟦	🟦	🟦	🟦*								
	Task 1B-2: The role of redox cycling on actinide mobilization in sediments		🟪	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦*		
	Focus Area 1C: NNSS E-Tunnel pond actinide migration												
	Task 1C-1: Characterization of E-Tunnel pond actinide profiles					🟩	🟦	🟦	🟦	🟦	🟦	🟪	🟪*
	Task 1C-2: Advective transport through pond sediments							🟩	🟩	🟦	🟦	🟦	🟦a
	Focus Area 1D: SRS pond B radionuclide cycling between sediments and surface water												
	Task 1D-1: Characterization of Pond B actinide profiles				🟦	🟦	🟦	🟦	🟦	🟦	🟦*	🟩	🟩
	Task 1D-2: The role of microbial activity on redox cycling and Pu mobilization					🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦a
	Focus Area 1E: SRS Radflex facility long-term actinide migration experiment												
	Task 1E-1 Characterization of actinides source composition and distribution in lysimeter coupons			🟦	🟦*							🟦	🟦a
THRUST 2: FUNDAMENTAL PROCESSES – ACTINIDE STABILIZATION AT ENVIRONMENTALLY RELEVANT TIMESCALES	Focus Area 2A: Actinide incorporation into mineral precipitates												
	Task 2A-1: Pu incorporation in iron oxides and calcium carbonate	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦*				
	Task 2A-2: Formation of actinide-Al solution complexes			🟩	🟩	🟦	🟦	🟦	🟦*				
	Focus Area 2B: Actinide aging on mineral surfaces												
	Task 2B-1: Actinide stability on Fe oxide and clay minerals during Fe(II) induced dissolution	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦*				
	Task 2B-2: Actinide remobilization following re-oxidation of anoxic sediments							🟦	🟦	🟦	🟦	🟦	🟦*
	Task 2B-3: Isotopic fractionation of Pu during sorption			🟩	🟩	🟪	🟪*			🟦	🟦a		
	Focus Area 2C: Microbial influences on actinide stabilization and mobilization												
	Task 2C-1: Characterization of microbial exudates and their interaction with Pu	🟩	🟩	🟦	🟦*								
	Task 2C-2: Pu mobilization from mineral surfaces by low-molecular weight microbial exudates			🟩	🟩	🟦	🟦	🟦	🟦*				
	Task 2C-3: Pu stabilization by microbial macromolecules on mineral surfaces transformation and complexation							🟦	🟦	🟦	🟦	🟦	🟦*
	Task 2C-4: Pu incorporation into iron oxides of microbial origin									🟦	🟦	🟦	🟦a

4.a Review of Scientific Progress

4.a.i Brief Review of Scientific Progress

Research Thrust 1: Field Studies— Biogeochemical Processes Affecting Actinide Transport in the Environment

Thrust 1 Coordinator: M. Zavarin

Thrust 1 focuses on investigating the role of kinetically slow and/or irreversible processes by examining the long-term behavior of actinides in the field and at sites with long histories of actinide contamination. Four field sites plus one engineered field site have been chosen based on their known contamination history, their range of contaminant loading, their location within watersheds, and the specific processes that are believed to control actinide transport (Table 2). These field sites allow us to test our conceptual and mechanistic understanding of actinide migration using long-term field-specific contaminant migration information. Each site is intended to test specific processes that may influence the long-term evolution of actinide mobility in the environment.

Table 2. Summary of the field sites. These field sites are both important practical areas and representative of key scientific challenges that face actinide contamination sites worldwide.

Site Location	Source History	Source Type	Depositional Environment	Geochemistry
Hanford Z-9 Trench WA	1955-1962 2,180 Ci $^{239/240}$Pu 1060 Ci ^{241}Pu 565 Ci ^{241}Am	Liquid waste disposed in unlined trench. Waste associated with HNO_3, HF, CCl_4, and TBP.	Semi-arid/desert climate (7 inches precipitation p.a.); Contamination beneath trench in vadose zone	Acidic waste (~pH 2.5), High Na nitrate, High organic compounds: CCl_4; TBP.; Oxic.
Sellafield/Ravenglass Estuary, Irish Sea UK	1952-Present 3,240 Ci ^{238}Pu; 16,500 Ci $^{239/240}$Pu; 590,000 Ci ^{241}Pu; 14,600 Ci ^{241}Pu; 240 Ci ^{237}Np	Treated waste discharged to Irish Sea. Actinides associated with iron flocs > 22 µm or in colloidal phase > 3 kDa.	Maritime climate (40 inches precipitaion p.a.); Tidal estuary; Silt and clay sediments deposited in low energy salt marsh	High organic content. Sediments rapidly become anoxic. Mixture of saline and freshwater
NNSS E tunnel ponds NV	1957-Present 0.04 Ci Pu	Discharge from weapons testing tunnels. Pu associated with colloids and organic matter	Subtropical hot desert climate; Artificial storage pond; Quaternary alluvium overlying fractured carbonate bedrock	High organic content. Clays and zeolite colloids; Oxic.
SRS pond B SC	1961-1964; 0.01 Ci ^{239}Pu	Liquid discharges of fuel element cooling waters.	Humid subtropical climate (40 inches precipitation p.a.); Artificial storage pond.	High organic content; Fe rich sandy sediments; pH = 5; Seaonal anoxia.
RadFlex SRS SC	2012-Present; 0.013 Ci $^{239/240}$Pu divided into 18 field lysimeters	Well characterized Pu sources placed in field lysimeter experiments	Pu sources placed in lysimeters; Left open for natural rainfall, atmospheric, and temperature fluctuations	Oxic, unsaturated zone, highly-weathered sandy loam/sandy clay loam soil, pH ~5

This Research Thrust is guided by the following overarching hypothesis:

Thrust 1 Hypothesis: *Biogeochemical processes occurring on the timescale of years to decades lead to greater actinide recalcitrance in sediments and limits their migration in surface and groundwater.*

Focus Area 1A: Hanford Z-9 vadose zone actinide migration

Lead: A. Kersting, contributors: S. Hellebrandt, V. Freedman, C. Pearce, K. Cantrell, N. Wall, I. Neil and E. Maulden

Hypothesis: *Organic solvents and acidic pHs lead to Pu mobilization in solution and minimal retardation. However, acid neutralization and mineral alteration over time leads to Pu sorption to native and alteration minerals and limits further transport.*

Located on the Columbia River, the Hanford Site, WA was established in 1943 to produce Pu for the Manhattan Project and actively reprocess Pu for nuclear weapons from 1944-1989. During its operation, approximately 4.44×10^{14} Bq (~12,000 Ci) of ^{239}Pu- laden liquid waste from both nuclear reactors and reprocessing of the waste streams were released to over 80 unlined shallow subsurface trenches, and pond disposal locations (Cantrell, 2009; Felmy et al., 2010). The vast majority of the Pu waste (~88-95%) was disposed of in the Plutonium Finishing Plant (PFP) in Area 200 where weapons-grade Pu metal was produced from Pu-containing nitrate solutions (Table 2). The unlined Z-9 trench received large volumes (~4x10^6 liters) of this waste consisting of high salt (~ 5M NO_3, ~ 0.6M Al), acidic (pH ~ 2.5) solutions, which also contained the organic solvents: CCl_4, TBP, DBP, and lard oil. Most of the Pu precipitated immediately within the first decimeters of the trench as PuO_2 and Pu-polymers or -hydroxides (Ames 1974, Price & Ames, 1975). However, a small fraction migrated deep into the subsurface vadose zone to depths of 37 m. A correlation between Pu and organic components was found in some cases (Cantrell & Riley, 2008), as well as correlation with Fe and P (Buck et al., 2014). The buffering capacity of the sediments and mineral dissolution (Ames, 1974) created diverse pH conditions in the subsurface, ranging from pH 2 to 8 (Cantrell & Riley, 2008). Pu interactions with the waste stream solution and sediment components are transient and include mineral dissolution, precipitation, and fluid composition changes over time. However, the mechanisms controlling subsurface migration are not well understood.

There are three tasks in Focus Area 1A all designed to identify the Pu migration mechanisms and develop predictions of Pu mobility and potential groundwater contamination at environmentally relevant timescales beneath the Z-9 trench. The first two tasks were initiated this year: Task 1A-1, Pu complexation with reprocessing waste, and Task 1A-2, reactions between sediments and Pu reprocessing waste. Task 1A-3, Pu reprocessing waste reactive transport through sediments, will begin in FY20 and build on the data obtained in Task1A-1 and -2.

Task 1A-1: Pu complexation with reprocessing waste

Task 1A-1 focuses on identifying which components of the waste stream have an influence on Pu migration. Results from this task will be used in the subsequent two other tasks. The major components of the waste stream that have been previously identified are various actinides and fission products, Al, nitrate, kerosene, carbon tetrachloride (CCl_4), tri-*n*-butyl phosphate (TBP) and its degradation products. Our initial focus is on the influence of high Al content in these sediments and determining if co-precipitation of Al and Pu occurs under salt-rich conditions.

Two series of batch experiments were carried out. The first was to monitor the precipitation of Al hydroxide as function of pH (2-8) in an Al (0.6 mol/L) and Na (5 mol/L $NaNO_3$) rich solution. In the second series of experiments, Pu(IV) (1×10^{-9} mol/L) was added to the system. In the Pu-free experiments, the cation concentration of the solution of each sample was measured at the designated pH with ICP-OES (Al^{3+}, Na^+) as a function of time up to 60 days. Al-oxy-hydroxide precipitation occurred by pH 4 and all of the Al had precipitated out of solution by pH 5, as expected (Figure 2, right). XRD measurements revealed that the Al precipitates were either amorphous or bayerite ($Al(OH)_3$). In the second set of experiments the Pu was measured by LSC after 12 days. It generally followed the Al, although some Pu remained in the aqueous phase for a given pH (Figure 2, left). The Pu was removed from solution as either a sorbed species to the Al-oxy-hydroxide or as a co-precipitate.

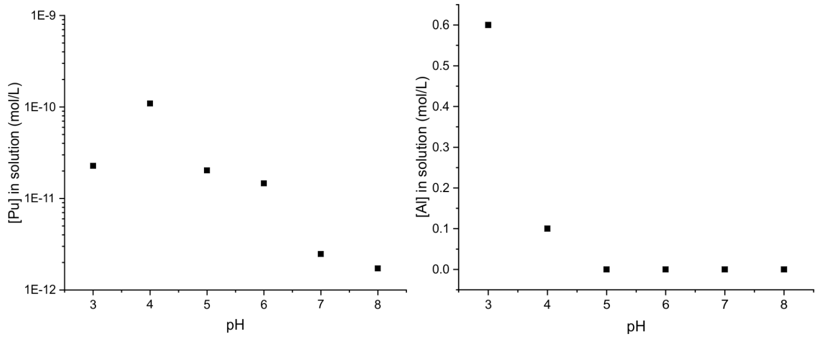


Figure 2. Aqueous Pu and Al concentrations in solution during simulated waste base titration.

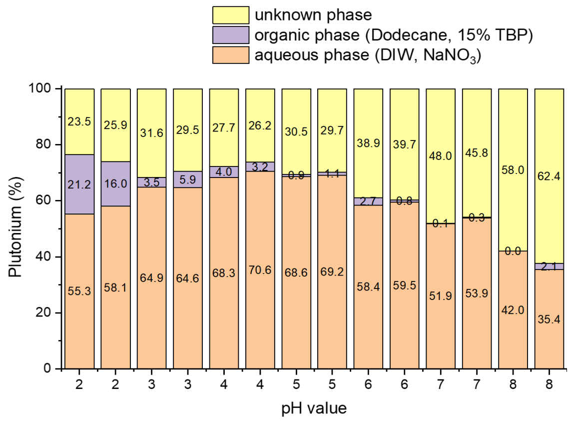


Figure 3. Pu distribution (%) between the aqueous (5 mol/L $NaNO_3$), organic (dodecane, 15% TBP) and an unknown phase after 30 d of equilibration as a function of pH, prepared as duplicates. Duplicates are plotted.

One of the organic solvents components in the RECUPLEX and the PUREX process used to recover Pu is tri-*n*-butyl phosphate (TBP). It is used to sequester Pu from the aqueous phase into the organic phase. In an effort to evaluate the influence of TBP on the Pu migration behavior, we carried out a series of binary batch experiments between an aqueous phase and an organic phase as a function of pH (2 to 8). The organic phase was dodecane (analog to kerosene) with and without TBP. Plutonium(IV) (10^{-10} M) in either water or nitrate (5M) was placed in contact with dodecane. After 30 days, Pu was measured in both phases using the LSC. At all pHs investigated, the Pu remained in the aqueous phase, as expected. In a follow-on experiment, TBP (15%) was added to the dodecane and the experiments were repeated. Under these conditions, a significant amount of Pu was sequestered into the organic phase at pH 2. However, at higher pH values only a minor amount of Pu was in the organic phase (Figure 3). A significant part of the Pu is present in neither the aqueous nor the organic phase. We continue to investigate whether the missing Pu is sequestered at the aqueous-organic interface.

Task 1A-2: Reactions between sediments and Pu reprocessing waste

Although it is believed that a major contribution to the transport of Pu and other radionuclides at the Z-9 trench is facilitated by the initial low pH and high organic content of the waste, the chemical reactions between the solution and sediments may also be important.

Based on the results from Task 1A-1 we are investigating the competition between Pu, the organic phase, and sorption to different mineral phases. Ternary experiments (aqueous-organic-mineral phase) were carried out with similar design to the experiments of Task 1A-1. Initially we focused on the feldspar, albite, a dominant mineral in surface soils. We will expand this effort to include pyroxene groups, and native Hanford sediments (in collaboration with PNNL).

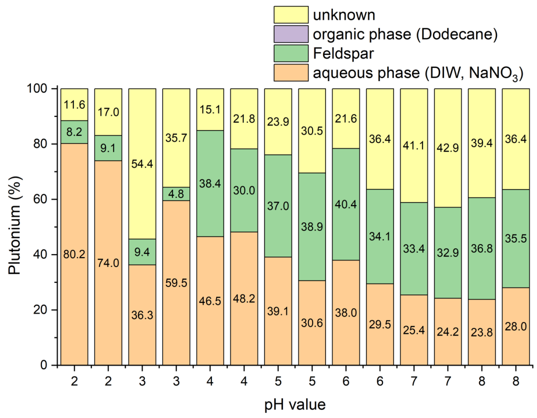


Figure 4. Pu distribution (%) between the aqueous (5 mol/L $NaNO_3$), organic (dodecane), mineral (Albite) and an unknown phase after 30 d of equilibration as a function of pH, prepared as duplicates.

Albite, the sodium end member of the alkali feldspar family ($Na[AlSi_3O_8]$), was used in the first set of experiments. The initial concentration of Pu(IV) in the aqueous phase was 1×10^{-10} mol/L. The maximum surface sorption of Pu onto the feldspar (1 g/L, grain size between 45 and 90 μm) was between 30% and 40% above pH 4 and expectedly lower below pH 4 (Figure 4). Our data show that no Pu was sequestered in the organic, as expected. A significant fraction of the Pu is present in neither the aqueous nor the organic phase and we are still working to understand if the Pu is sequestered at the aqueous-organic interface. Follow-on experiments will investigate the behavior of Pu with the addition of 15% TBP in the organic phase.

Task 1A-3: Pu reprocessing waste reactive transport through sediments

We have begun planning experiments for FY20. The goal is to design a series of column transport experiments using native Hanford sediments and simulated Z-9 reprocessing waste solutions to mimic the geochemical evolution of Pu transport in the vadose zone beneath the Z-9 trench. To date we focused on developing a collaboration with staff scientists at PNNL who are working on characterization of surface sediments at the Z-9 trench. We have monthly teleconference calls, have identified the soil samples to be use and our colleagues from PNNL have shipped soil samples for us to use. The design and development of sediment column transport experiments has been supported by discussions with Dr. Tetsu Tokunaga (LBNL) who has a wealth of experience performing similar experiments as part of the LBNL SFA.

Focus Area 1B: *Ravenglass/Sellafield radionuclide migration in estuary sediments*

Lead: E. Balboni, contributors: F. Quinto H. Geckeis, G. Law, S. Tumey, and N. Merino

Hypothesis: *Actinide distributions in estuary sediments reflect the discharge history from the Sellafield reprocessing plant and their low mobility in reducing sediments. Desorption and diffusion will be affected by changes in redox conditions; oxidation of reduced mineral phases containing Fe(II) and formation of Fe(III) precipitates will result in sequestration of U, Np, Pu and Am.*

The Sellafield site on the north west coast of England was originally established in 1947 to support the UK nuclear weapons program (Figure 5). Since 1952, authorized liquid radioactive effluents have been discharged from the Sellafield plant into the Irish Sea. This is, by far, the largest source of Pu discharged in all of western Europe with 276 kg Pu released. In the Eastern Irish Sea, the majority of the transuranic activity has settled into an area of sediments ("Mud Patch") off the Cumbrian coast. The radionuclides from the mud-patch have been re-dispersed via particulate transport in fine-grained estuarine and intertidal sediments in the North-East Irish sea (Hamilton and Clarke, 1984; Kershaw et al., 1995; Mackenzie et al., 1994) including the Ravenglass estuary (Burton and Yarnold, 1988; Caborn et al., 2016; Lucey et al., 2004; Mackenzie and Scott, 1993; Mackenzie et al., 1994). The Ravenglass saltmarsh is located 10 km south of the Sellafield site and is a low energy, intertidal region that accumulates Sellafield-derived contamination (Hamilton and Clarke, 1984). The Ravenglass estuary presents a unique natural laboratory in which to study the long-term biogeochemistry of anthropogenic radionuclides under natural environmental conditions. Salt marshes like Ravenglass are highly dynamic systems which are vulnerable to external agents (Adam, 2002) (sea level changes, erosion, sediment supply and fresh water inputs), and there are uncertainties about their survival under current sea level rises and possible increases in storm activity (Leonardi et al., 2016; Temmerman et al., 2004). Despite periodic study over the past several decades, understanding of the biogeochemical controls on long-term radionuclide distribution and retention at Ravenglass remains limited. Recent work has indicated redox conditions shift from aerobic at the surface, to Fe(III) reducing within 12 cm depth, and sulfate reducing between 18-28 cm. Changing redox profiles together with changing hydrological regimes have the potential to impact the speciation and mobility of the redox active radionuclides, including Pu.

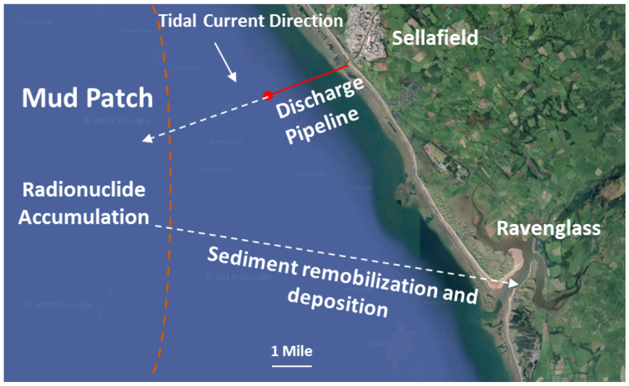


Figure 5. Location of the Ravenglass Estuary showing conceptual model of discharge of radioactive waste, and subsequent remobilization of the mud patch sediments and deposition in the Ravenglass Estuary (Mccartney et al., 1994; Reynaud and Dalrymple, 2012)

There are 2 tasks in Focus Area 1B that were part of our efforts beginning in 2017. Task 1B-1 is to characterize a sediment core from Ravenglass we collected in FY18 and produce an actinide profile. The second task, Task 1B-2 is to investigate the role of redox cycling on actinide mobilization within the Ravenglass sediment core.

Task 1B-1: Characterization of Ravenglass estuary actinide profiles

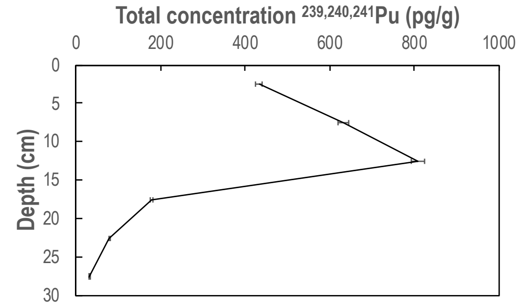


Figure 6. Spatial distribution of total ^{239,240,241}Pu in the Ravenglass sediment cores.

The sediment core collected from the Ravenglass saltmarsh in 2017 is 30 cm in length and was shipped to LLNL where it is stored under controlled conditions. It was divided into six 5-cm layers and sub-aliquots were prepared to determine the vertical distribution of radionuclides (Pu, Am and Cs) in the sediment column. Approximately 0.2 g of each sediment section was digested via total acid dissolution and prepared for analysis via multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). In the sediment core, Pu reaches a maximum concentration at a depth layer of 10–15 cm (Figure 6, Table 3); the Pu concentration drops significantly below 15 cm. Additionally, these data show that ^{240}Pu/^{239}Pu ratio changes with depth. We are currently reviewing historic Sellafield discharge records to determine if changes in Pu isotopic ratios with sediment depth reflect historic changes in Sellafield discharge history. The ^{241}Am and ^{137}Cs content was determined via gamma spectroscopy (Figure 7). The peak activity (Bq/g) for ^{137}Cs and ^{241}Am is at 5-10 cm depth, which differs from Pu distribution where peak concentration found at 10-15 cm depth. These changes in radionuclide peak concentrations with depth may highlight differences in radionuclide migration within the sediment column. We will compare our measured concentrations with known Sellafield discharges.

Table 3. ^{240}Pu/^{239}Pu ratios in the Ravenglass sediment core

Depth	^{240}Pu/^{239}Pu
0-5 cm	0.2048±0.0004
5-10 cm	0.2061±0.0004
10-15 cm	0.1371±0.0004
15-20 cm	0.1445±0.0004
20-25 cm	0.1965±0.0004
25-30 cm	0.1982±0.0004

X-ray powder diffraction (P-XRD) was conducted on the 5–10 cm sediment sample. The sediment mainly consists of chlorite, quartz and muscovite (data not shown). X-ray fluorescence (XRF) data will be gathered to determine major and minor element composition of each sediment layer.

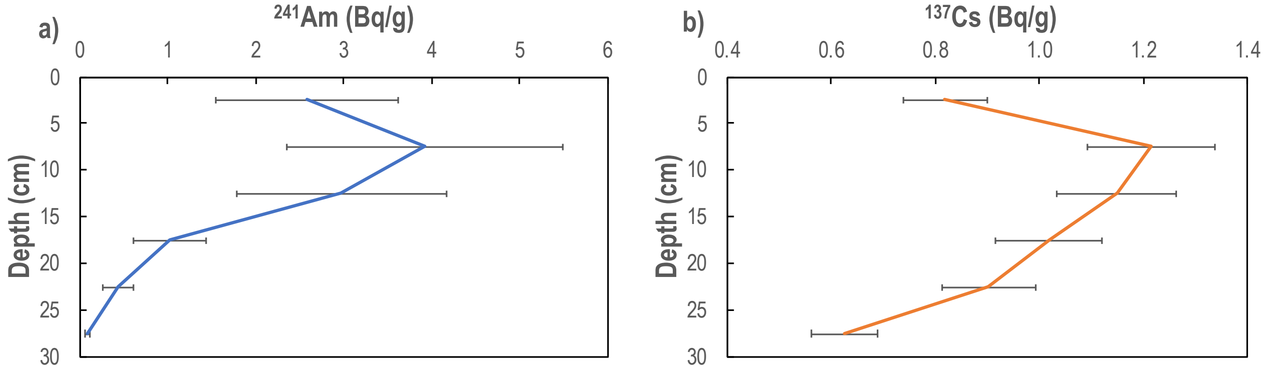


Figure 7. Spatial distribution of ^{241}Am (a) and ^{137}Cs (b) in the Ravenglass sediment cores.

Task 1B-2: The role of redox cycling on actinide mobilization in sediments

The goal of this task is to examine the factors affecting the mobility of Pu in redox stratified sediments by conducting desorption experiments of contaminated Ravenglass sediments under both oxic and anoxic conditions. Desorption experiments were conducted over an eight-month period. The anoxic desorption experiments have been completed and were conducted in a Coy anerobic chamber and sampling occurred after 1, 22, 85 and 239 days. Atmospheric (oxic) desorption experiments are currently underway and sampling was completed after 1 and 22 days. The oxic experiments were started in an anaerobic chamber and subsequently moved to atmospheric conditions—bottles capped with porous bungs, shaken daily. In all the desorption experiments, Ravenglass sediments from each layer were mixed with degassed artificial seawater (ASW) to yield 10 g/L suspensions. The experiments were periodically sampled to determine the amount of desorbed Pu via MC-ICP-MS – (Multi Collector Inductively Couple Mass Spectrometry) and redox indicators (Eh, pH and extractable Fe(II)). In the anoxic desorption experiments, reducing conditions were maintained during the entire sampling period of 282 days with Eh ranging between -400 and -200 mV. In the oxic experiments at day 22 the Eh ranged between 300 and 800 mV, indicating that upon exposure to the atmosphere the sediment suspensions have become more oxidizing compared to the anoxic experiments. At each sampling point in both the anoxic and oxic experiments, the Fe(II) ingrowth was measured. This solid phase chemical extraction has been shown to extract microbially derived Fe(II) and is an indictor of the reducing potential of the sediment (Lovley and Phillips, 1986).

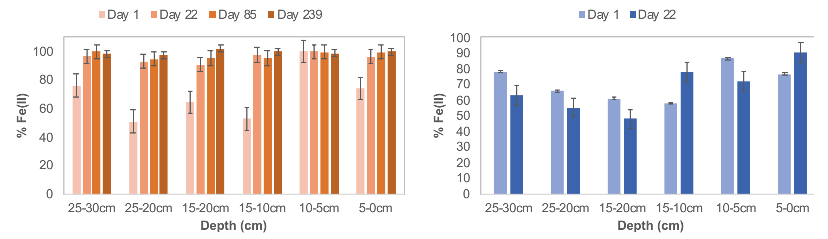


Figure 8. Ingrowth of Fe(II) to sediments determined via 0.5N HCl extraction in anoxic (left) and oxic (right) desorption experiments.

In the anoxic experiments, there is a 10–30% ingrowth of Fe(II) in all sediment layers from day 1 to day 22 (Figure 8). In contrast, in four of the soil suspensions in the oxic experiments the amount of ingrown Fe(II) sediments decreases 10-20%. We will keep monitoring Eh and Fe(II) in the oxic experiments to understand the oxidizing and reducing potential of the sediment layers and how they relate to Pu (and other radionuclide) desorption.
So far, we have processed two desorption solutions from the oxic experiments (85 days) to determine Pu desorption behavior. Results show that more Pu is desorbed from the 15–20 cm layer compared to the 5–10 cm layer (Table 4). Overall the Pu isotopic signature measured in the desorbed solutions is consistent with the Pu isotopic ratio of the layers in the sediment core.

Table 4. Pu concentration and isotopic ratios measured from desorption solution (anoxic, day 80)

Layer depth	$^{240/239}$Pu	Pu desorbed (pg)
5-10 cm	0.2042 ± 0.002	0.05
15-20 cm	0.1596 ± 0.004	0.12

Parallel to the preparation of samples for Pu analysis via MC-ICP-MS, we are developing a sample preparation method to conduct multi-actinide measurements via Atomic Mass Spectrometry (AMS). AMS analysis of desorption solutions should allow for a more comprehensive understanding of actinide desorption behavior from Ravenglass sediments, complementing the Pu data obtained via MC-ICP-MS.

The composition of the microbial community at both the beginning and end of the desorption experiments is being characterized. The community profiles were obtained by 16S rRNA sequencing of the V4 region and processed through Dada2 and Phyloseq. For example, Figure 9 shows the microbial communities for each soil layer collected at the end of the anoxic desorption experiments (239 days, all layers). The microbial community in these samples mainly consists of halophiles and sulfate-reducing bacteria, consistent with what is expected for Ravenglass sediments (Newsome et al., 2014). Other potential metabolisms include anaerobic heterotrophy

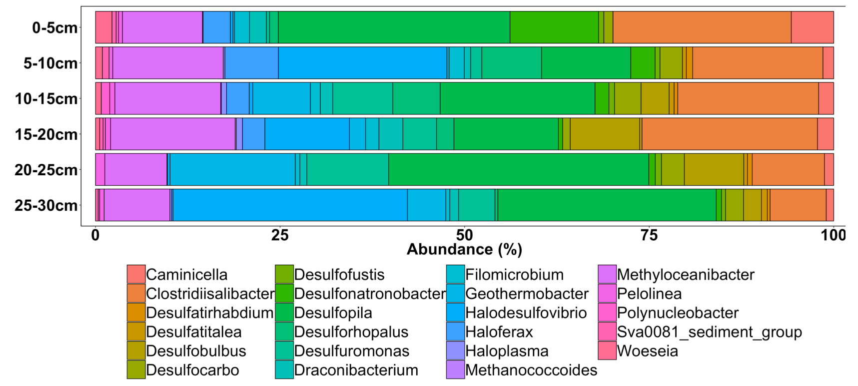


Figure 9. Genera-level composition of the microbial community in anoxic sediment slurries after 8 months incubations.

(e.g., Caminicella), methanogenesis (e.g., Methanococcoides, Pelolinea), and methylotrophy (e.g., Methyloceanibacter).

The results of this work are providing information on the potential mobilization of actinides in biogeochemically dynamic/transient environments over long timescales. Understanding the behavior of actinides in such conditions remains a significant challenge and will ultimately help to develop predictive conceptual and numerical models of actinide mobility in the environment.

***Focus Area 1C**: NNSS E-Tunnel pond actinide migration*

Lead: M. Zavarin; contributors: N. Merino, post-doc (TBD)

This project will commence in mid FY20. To initiate this effort, we reached out to Duane Moser (DRI) to discuss microbiological aspects of this new effort. Nancy Merino is leading those discussions and, as part of this effort, is evaluating the microbiota that may be relevant at this site. A manuscript was recently submitted that identifies a unique deep subsurface microbe at the NNSS (see science highlights) and a second manuscript examining the groundwater microbial communities of southern Nevada is in preparation.

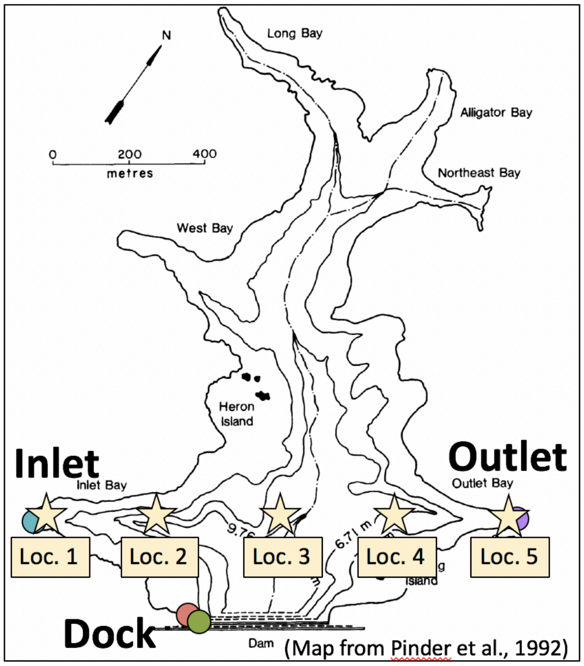
***Focus Area 1D**: SRS Pond B radionuclide cycling between sediments and surface water*

Lead: B. Powell, contributors: N. Merino, Y. Jiao, K. Peruski, D. Kaplan

***Hypothesis:** Seasonal anoxia leads to remobilization of Pu from shallow sediments into overlying water due to linkages with Fe-oxide dissolution and organic matter mobilization resulting from changes in microbial activity, release of cellular exudates, and changes in pore fluid redox conditions.*

SRS Pond B at Savannah River Site is an ideal location for examining the biogeochemical cycling of Pu. This pond received inputs of ^{238,239,240}Pu, ^{137}Cs, ^{90}Sr, ^{241}Am, and ^{244}Cm from SRS R reactor cooling water between 1961–1964 (Whicker et al. 1990). Since then, Pond B has remained relatively isolated except for a few studies conducted in the late 1980s, demonstrating Pu cycling with seasonal anoxia (Alberts et al. 1987; Pinder et al. 1992; Whicker et al. 1990). However, the mechanism(s) causing Pu mobilization are still unknown. The objective of Focus Area 1D is to evaluate the Pond B actinide profiles (both in the water and sediment columns) and determine the biogeochemical factors that influence Pu mobility and seasonal radiologic fluxes between the sediments and overlying pond water.

This Focus Area 1D has two tasks. The focus of the first task is to initiate a field sampling program to examine the biogeochemical cycling of Pu, which was deposited in the pond sediments over 50 years ago. The second task (Task 1D-2) is to investigate the microbial influence on the redox cycling and Pu mobilization in the sediments and pond water. Task 1D-2 will commence in FY20.



(Map from Pinder et al., 1992)

Figure 10. Map of Pond B sampling locations. Colored circles indicate locations sampled in February 2019 and colors match with Figure 11. Stars indicate sampling locations throughout the full-scale sampling between June 2019–2020.

Task 1D-1: Characterization of Pond B actinide profiles

In February 2019, we conducted a small-scale field sampling campaign as part of the planning process for establishing Pond B as an experimental field site. We collected water and sediment cores for actinide/radionuclide concentrations and microbial community profiling. Water was collected at 4 locations

(Western Inlet, Western Shore, Central Dock, and Eastern Outlet) and sediment cores collected at 1 location (Central Dock) (Figure 10).

The actinide and radionuclide concentrations are listed in Table 5. These are the first records of ^{137}Cs, ^{214}Pb, ^{214}Bi, ^{226}Ra/^{235}U, and ^{40}K in the water column at Pond B. The high concentration of ^{137}Cs in the Western Inlet is due to inadvertent mixing of the water column with sediment. Indeed, ^{137}Cs in Pond B was previously observed to reside in surface layers of littoral zone sediment (< 30 Bq/g dry mass), even after 20 years had passed since input from R reactor (Pinder et al. 1995; Whicker et al. 1990). The ^{137}Cs is an important radionuclide to understand in Pond B, as it was previously shown to strongly correlate with ^{239,240}Pu concentrations in sediment (Whicker et al. 1990). Plutonium analysis of these ponds waters will be performed later this year.

Table 5. Concentrations of actinides and radionuclides in water samples collected at about 0.6 m depth during the reconnaissance field sampling campaign (February 2019).

Activity (Bq/L)	Western Inlet[a]	Western Shore	Central Dock	Eastern Outlet
^{137}Cs	16.58	0.44	0.31	0.03
^{214}Pb	0.19	0.32	0.12	0.06
^{214}Bi	0.04	nd	nd	nd
^{226}Ra/^{235}U	1.11	4.64	2.43	nd
^{40}K	1.28	3.22	0.16	0.38

[a] Large particulates and sediment were collected in the Western Inlet water samples; nd = not detected

We analyzed the microbial community profile of Pond B in the water column and sediment (Figure 11). These data are currently being used to develop the plan for Focus Area 2C-1 to understand the microbial influence on Pu cycling. In Pond B, there are a wide variety of microbial metabolisms, including photosynthesizers, heterotrophs, fermenters, methanotrophs, methanogens, iron oxidizers, and iron reducers. These microorganisms likely release different extracellular exudates with a range of Pu binding affinities, influencing Pu mobility.

In our sampling campaign planned for June 2019–2020, we will monitor actinides/radionuclides and various biogeochemical parameters at Pond B over time at 5 locations (Figure 10). We will measure water column profiles of 11 parameters in real-time with a conductivity-temperature-depth (CTD) probe. We will also conduct full biogeochemical profile characterization of actinide, trace metals, major ions, tritium, total inorganic and organic carbon, and microbial community in the water column (1 m intervals), sediment (approximately 20 cm cores), and sediment pore water fluid. All the data collected will be uploaded to ESS-DIVE as part of our Data Management Plan.

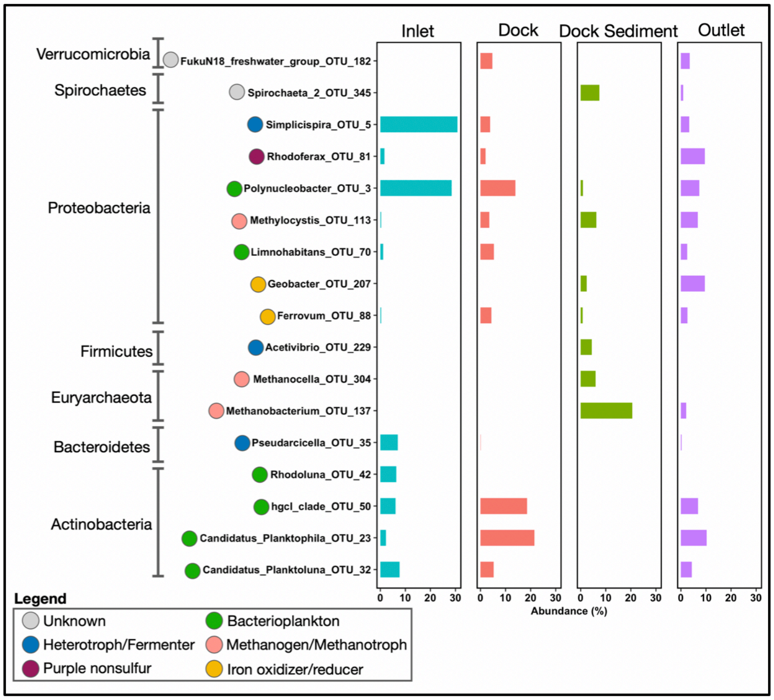


Figure 11 Microbial community profile of Pond B. The legend describes the different microbial metabolisms present in Pond B. The profile represents 16S rRNA amplicon sequencing, and the bar plot depicts OTUs (operational taxonomic unit) present at > 4% abundance in at least one sample.

Focus Area 1E: SRS Radflex facility long-term actinide migration experiment

Lead: B. Powell, contributors: D. Kaplan, M. Maloubier, E. Balboni

Hypothesis: *The reaction rates that ultimately control actinide transport can be slow and/or irreversible. As a result, the sources can retain a signature of their depositional history over a timescale of decades.*

This long-term field project, started in 2012, involves characterizing the redox and transport behavior of the Pu sources deployed in a field lysimeter experiment at the Savannah River Site (RadFLEx: Radiological Field Lysimeter Facility), which is currently operated by Dr. Daniel Kaplan of the Savannah River National Laboratory and Dr. Brian Powell at Clemson University. The lysimeters are 24” tall by 4” diameter PVC columns packed with soil from the SRS and with a Pu bearing source (~2 mg of a solid sample placed between two glass fiber filters) placed midway in the lysimeter during soil packing. Of the 48 deployed lysimeters, 18 have Pu sources containing $Pu^{III}_2(C_2O_4)_3(s)$, PuO_2 nanocolloids, $Pu^V(NH_4)(CO_3)(s)$ (with and without organic matter amended to the soil), and $Pu^{IV}(C_2O_4)_2(s)$. We deployed all sources in triplicate. Triplicate lysimeters for each of these sources are currently in the field with plans to remove them at three time intervals: 4 years, 7 years, and 20 years.

Focus Area 1E has 1 task designed to characterize the actinide source composition and vertical distribution of Pu in the lysimeters. In FY19, the 4-year lysimeter samples were removed and characterized. Samples were destructively sampled to determine the Pu concentration in soil as a function of distance from the source. The source material was recovered and analyzed for its chemical and physical speciation.

Task 1E-1: Characterization of actinides source composition and distribution in lysimeter coupons

We previously reported that samples from the $Pu^{III}_2(C_2O_4)_3(s)$, $Pu^V(NH_4)(CO_3)(s)$, and $Pu^{IV}(C_2O_4)_2(s)$ sources all underwent a transformation to a distorted $PuO_{2+x-y}(OH)_{2y}\cdot zH_2O$ type structure. Analysis of Pu sources initially deployed as $PuO_2(s)$ colloidal particles had a similar distorted $PuO_{2+x-y}(OH)_{2y}\cdot zH_2O$ type structure. The EXAFS spectra (Table 6) obtained for the source deployed in the lysimeter as well as a second source which was archived in the laboratory under an inert atmosphere, are similar with PuO_2 colloids and slightly shorter Pu-O and Pu-Pu distance compared to bulk PuO_2 (Ekberg *et al.*, 2013). These data indicate a steady transformation of Pu sources from various initial conditions to a disordered $PuO_{2+x-y}(OH)_{2y}\cdot zH_2O$ type phases over time.

Table 6: EXAFS data on Pu and Np in both the archived sources and field exposed lysimeter data (grey).

	First shell	Second shell	Third shell
PuO_2 crystal structure	7 O at 2.34 Å	-	9 Pu at 3.82 Å
PuO_2 colloidal particles	8 O at 2.294 Å	-	3.9 Pu at 3.793 Å
PuO_2 colloidal particles s^2 (Å^2) =	6.3 O at **2.31(1)** Å 0.008	1.7 O at **3.30**(1) Å 0.01	4.2 Pu at **3.80(1)** Å 0.005
Lys44: PuO_2 colloidal particles s^2 (Å^2) =	6.3 O at **2.31(1)** Å 0.009	1.7 O at **3.31**(1) Å 0.008	4.4 Pu at **3.79(1)** Å 0.006

To test the field observations of the formation of stable $PuO_{2+x-y}(OH)_{2y}\cdot zH_2O$ phases under a variety of conditions, laboratory studies were conducted monitoring Pu sorption to SRS soil and kaolinite (dominant clay mineral in SRS soil). The goal was to determine the conditions where formation of $PuO_{2+x-y}(OH)_{2y}\cdot zH_2O$ occurs. Plutonium, initially as Pu(VI), reacted with SRS soil and pure kaolinite for 24 days to create samples containing Pu solid phase concentrations ranging from 1 to 3000 ug/g. Desorption experiments were then conducted to note differences in the desorption behavior as a function of Pu concentrations. This could indicate an influence of surface $PuO_2(s)$ type precipitates. Desorption of Pu from kaolinite and SRS soil from the 3000 ug/g doped samples were comparable. The XAS analysis indicated the presence of Pu-Pu bond distances in both samples signifying the presence of precipitates. High resolution transmission electron microscopy (TEM) analysis revealed

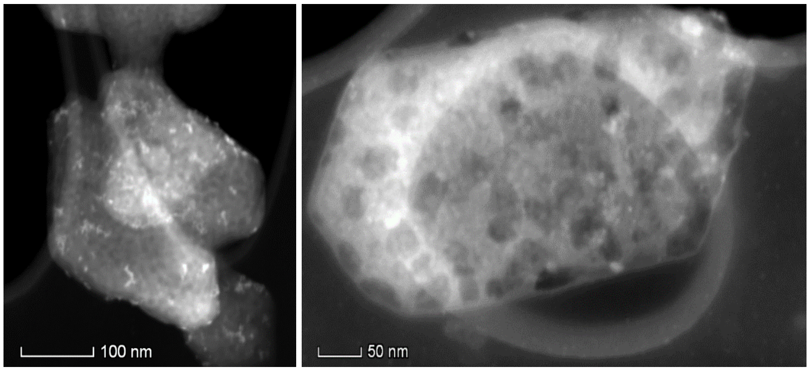


Figure 12: TEM images of kaolinite after reaction with Pu(IV) at 3000 μg/g$_{solid}$ (left) and SRS soil after reaction with Pu(IV) at the same concentration (right). Nanoprecipitates are clearly visible on the kaolinite surface in the pure kaolinite sample.

visible precipitates on the surface of the kaolinite (Figure 12). We are currently studying the reason for the difference in TEM observations.

Research Thrust 2: *Fundamental Processes: Actinides Stabilization at Environmentally Relevant Timescales*

Thrust 2 Coordinator: A. Kersting

Research Thrust 2 examines in detail the processes that may lead to long-term stabilization of actinides in sediments. In this SFA, we focus on three broad categories of stabilization which include co-precipitation of Pu in common minerals, the role of redox cycling on actinide stabilization on mineral surfaces, and the role of microorganisms and their exudates in actinide mobilization and immobilization. Each of the processes we investigate is of central importance to at least one field site. However, the processes of co-precipitation, surface reactions and microbial interactions are applicable across a wide range of hydrologic conditions. Research Thrust 2 is guided by the following broad hypothesis:

Thrust 2 Hypothesis: *Long-term biogeochemical processes include mineral and surface alteration which leads to stabilization of actinide surface associations or incorporation into mineral precipitates.*

Focus Area 2A: *Actinide incorporation into mineral precipitates*

Lead: E. Balboni, contributors: H. Mason, C. Booth, K. Smith

Hypothesis: *The extent of Pu incorporation into mineral phases is controlled by the nature of the substituting cation, mineralogical structural constraints, and competition with complexing ligands.*

Knowledge of the interactions of actinide ions with mineral surfaces is important for understanding its long-term environmental behavior. Iron (oxy)hydroxides are common soil minerals and are present in intermediate level of radioactive waste (Marshall et al., 2014). The study of interactions of Pu with mineral surfaces have thus far largely focused on simple sorption experiments (Begg et al., 2013; Lu et al., 1998; Powell et al., 2005b; Sanchez et al., 1985a). However, this is likely to oversimplify processes occurring in the environment. For example, Pu has a strong sorption affinity for Fe oxide minerals (Sanchez et al., 1985; Zhao et al., 2016), but Fe minerals in dynamic biogeochemical settings will likely be subject to dissolution and recrystallization. Under such a model, incorporation or co-precipitation reactions may offer a more meaningful insight into plutonium mobility in the long-term. Studies of Pu incorporation into minerals are limited. (Balboni et al., 2015; Heberling et al., 2008a; Heberling et al., 2008b; Heberling et al., 2011; Kelly et al., 2006; Meece and Benninger, 1993; Reeder et al., 2004; Reeder et al., 2001; Sturchio et al., 1998). Gaining a detailed understanding of the interactions between iron oxide and plutonium (Pu) is key in predicting the long-term stability and mobility of Pu in the natural environment.

There are two tasks associated with Focus Area 2A. Task 2A-1 was initiated in FY19 and the Task 2A-2 will begin in FY20. The first task focuses on understanding if Pu can co-precipitate with Fe-oxides and calcite. The second task explores the formation of actinide-Al solution complexes.

Task 2A-1: Pu incorporation in iron oxides and calcium carbonates

In the initial stage of this task, we are focusing our efforts in understanding interactions of Pu during co-precipitation with mixed Fe(II)/Fe(III) minerals. The synthesis of magnetite and green rust were optimized without Pu in an oxygen free glovebox and the nature of the synthesized materials was analyzed via P-XRD. The crystallinity and mineralogy of the mineral suspension (magnetite and green rust) were monitored for up to 60 days (Figure 13).

Once the synthesis was optimized, an aliquot of 1.3x10^{-3} M ^{242}Pu(IV) solution was added to the synthesis of magnetite and sulfate green rust, separately, to achieve a Pu concentration of ~500 ppm in the solid. In the magnetite system, >99.9% Pu was associated with the solid (pH of mother liquor between 8-9). In comparison, 95% of Pu was associated with the green rust solids, two hours after synthesis was completed (pH=8). Pu aqueous concentrations were measured for up to 60 days, but no significant changes were observed from the initial measurements. In both mineral systems Pu was overwhelming associated with the solid over the aqueous phase. Characterization of the structure of Pu associated with these mineral phases is underway using both TEM and X-ray absorption spectroscopy (XAS) at the Stanford Synchrotron Light Source in collaboration with C. Booth and K. Smith (LBNL).

Aliquots of Pu-doped mineral suspensions of magnetite and sulfate green rust were equilibrated with a degassed low ionic strength solution to make 10 g/L suspension. For each mineral suspension (green rust and magnetite) one set of samples was kept in the glovebox and a parallel set was exposed to oxygenated atmosphere conditions. Results indicate that magnetite maintains its crystallinity after 3 days of exposure to oxygenated atmosphere; however, sulfate green rust shows loss of crystallinity (data not shown).

After 24 hours and 3 days, aliquots of the mineral suspension (in oxic and anoxic experiments) were centrifuged (6000 rpm, 10 minutes) and the aqueous Pu in suspension was measured. After 3 days, 99.5% of Pu remains associated with the solid of both minerals under both anoxic and oxic conditions. We will monitor Pu desorption at day 10 and day 30. Solids at each step will be saved for EXAFS measurements. Changes in mineralogy in the oxic experiments are monitored by P-XRD. Importantly, these results suggest that intrusion of oxidizing conditions will not lead to the remobilization of Pu from reduced iron oxide phases. We plan to continue these experiments for at least six months.

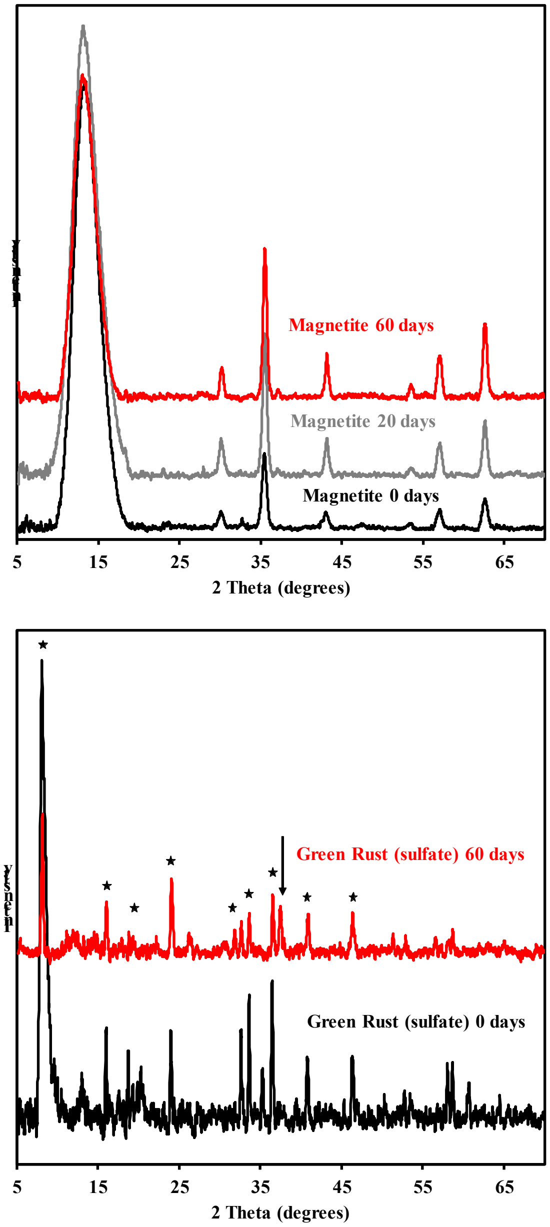


Figure 13. (Top) P- XRD of magnetite measured at 0, 20, and 60 days. The asterisks correspond to the powder diffraction file of magnetite # 01-071-6336; (Bottom) P-XRD of sulfate green rust measured at 0) and 60 days. The asterisks correspond to the powder diffraction file of sulfate green rust # 00-041-0014. The arrow indicates the presence of an additional phase identified as an $Fe_2(OH)_2$ (#00-013-0089).

Focus Area 2B: *Actinide aging on mineral surfaces*

Lead: Y. Jiao, contributors:, K. Morrison, C. Pan

Hypothesis: *Addition of Fe(II)$_{aq}$ to Fe oxide and montmorillonite minerals with sorbed Np and Pu will result in short term remobilization of the actinides due to reductive dissolution of the mineral phases. At long timescales, recrystallization reactions will result in a higher affinity of the actinides for the mineral surface. Oxidation of reduced mineral phases containing Fe(II) will result in a greater affinity of Np and Pu for the minerals due to the precipitation of Fe(III) solids and the incorporation of the actinides in these solids.*

Although typically poorly defined, the term "aging" is broadly used to describe surface processes that occur after initial sorption that cause changes in contaminant surface speciation over time (Tinnacher et al., 2011). In previous work in this SFA, we have focused on aging processes in binary actinide-mineral systems. In contaminated environments, however, mineral-actinide interactions occur in dynamic biogeochemical settings and accordingly may be subject to additional processes, such as microbially-mediated redox changes that are in a continual state of flux. We have previously demonstrated the importance of Pu redox speciation in binary mineral-actinide experiments (Begg et al., 2014; Begg et al., 2017; Begg et al., 2013; Zhao et al., 2016). In this Focus Area we now aim to bridge the gap between traditional microcosm experiments that provide evidence for environmentally relevant processes and controlled, binary, mineral-actinide experiments that provide mechanistic insights into these processes.

There are three tasks in Focus Area 2B all designed to explore 2 objectives: i) the extent to which aqueous Fe(II) can cause the desorption of actinides sorbed to mineral surfaces under anoxic conditions, and ii) how the actinides and Fe(II) behave following subsequent oxidation. Task 2B-1, Actinide stability on Fe oxide and clay minerals during Fe(II) induced dissolution, was initiated in FY19. Tasks 2B-2 and 2B-3 (Actinide remobilization following re-oxidation of anoxic sediments and Isotopic fractionation of Pu during sorption, respectively) will begin in FY20. By investigating the way in which Fe redox cycling controls Np and Pu mobility, we will gain a better understanding of the way the actinides behave in dynamic biogeochemical environments. By examining the role of Fe in experiments without microorganisms, we will understand the ways in which biotic processes can influence actinide mobility in Thrust 2, Focus Area 2C (Pu incorporation into iron oxides of microbial origin).

Task 2B-1: Actinide stability on Fe oxide and clay minerals during Fe(II) induced dissolution

Pu(V) can be reduced by either humic acid (Andre and Choppin, 2000) or by goethite upon adsorption (Powell et al., 2005a). Reduced Pu(IV) could form ternary complexes with HA and goethite or get incorporated into HA-iron oxide aggregates (Conroy et al., 2016). In natural environments, dissolved HA can be reduced by microorganisms via an electron transfer pathway (Lovley et al., 1996), and the resulting HA$_{red}$ can serve as an electron shuttle promoting iron oxide reduction and dissolution (Bauer and Kappler, 2009; Liao et al., 2017; Nevin and Lovley, 2002; Wolf et al., 2009). In this study, we examined the effects of reduced humic acid on the stability of Pu associated with goethite.

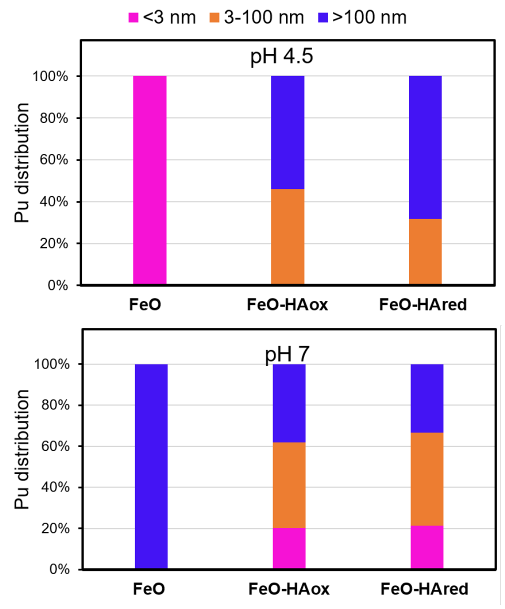


Figure 14. Pu distribution with 100 mg/L goethite and 10 mg$_C$/L HA in 0.005 M NaCl after 24 hours at anoxic conditions.

In a series of batch sorption experiments, HA$_{red}$ suspension was generated by Pd-catalysts in an anoxic glovebox to ensure strict anaerobic conditions. We quantified the Pu concentration in different size fractions (defined as < 3nm "aqueous", 3–100 nm "colloidal", and > 200 nm "particulate") when the reactions reached steady state (Figure 14). The distribution of Pu in the absence of HA indicated that complete adsorption to goethite was achieved at neutral pH and no adsorption occurred at pH

4.5, which is consistent with former studies (Powell et al., 2005a; Sanchez et al., 1985b). The presence of HA$_{ox/red}$ has a distinct effect on the Pu distribution among the three size fractions, which can be attributed to the complex interaction between HA, Pu and goethite. At pH 4.5 approximately 40% of Pu was associated with the colloidal fraction while the rest was associated with particulates. The large fraction associated with particulates may be due to the negatively charged HA which neutralizes some of the positive charge on the goethite surface at low pH allowing for aggregation to occur. The reduced Pu(IV) either adsorbs to goethite as a ternary surface complex or is incorporated into the aggregate particles. At pH 7, goethite is stabilized by HA due to enhanced electrostatic repulsion effects, resulting in more Pu in the colloidal or dissolved states.

Interestingly, the presence of HA$_{red}$ did not show distinct effects on Pu stability compared with HA$_{ox}$ at pH 4.5 and 7 even though the reducing capacity of HA$_{red}$ is much higher than HA$_{ox}$. This could be mainly due to two reasons: 1) HA$_{red}$ did not induce mineral phase transformation in the short term (Liao et al., 2017); or 2) Pu(V) can be quickly reduced to Pu(IV) by HA$_{ox}$ and HA$_{red}$ within two hours, which lead to similar adsorption behavior. We did not quantify the potential presence of Pu(III) in these experiments. The reduction of Pu(IV) to Pu(III) could lead to differences in Pu sorption behavior. Longer term experiments examining the stability of Pu in the presence of oxidized and reduced HA will be conducted in FY20.

Task 2B-2: Actinide remobilization following re-oxidation of anoxic sediments

Under anoxic conditions, Pu(V) can be reduced to Pu(IV) by humic acid and complexes may coexist with Fe(II). However, the redox conditions of subsurface environments are often disturbed. Oxygenation events that produce hydroxyl radicals through the interaction of O$_2$ with the reduced components, particularly Fe(II) (Minella et al., 2015; Page et al., 2013; Tong et al., 2015). The generation of hydroxyl radicals from oxygenation of anoxic sediments containing Pu(IV) may have a significant impact on the fate and transport of Pu.

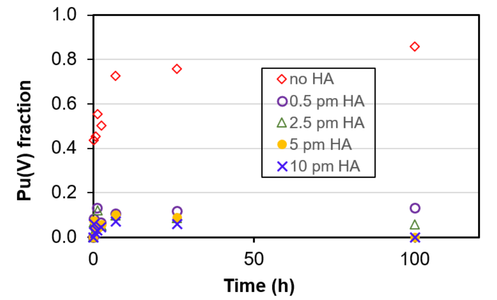


Figure 15.Pu(V) generation at pH 3.5 at oxic conditions. [Fe(II)]$_0$= 0.1 mM, [H$_2$O$_2$]$_0$= 0.1 mM, [Pu(IV)]$_0$=10^{-10} M.

In this study, we measured the oxidation state and stability of Pu when anoxic sediments containing Pu(IV)/HA/Fe(II) were exposure to H$_2$O$_2$. Without HA, significant oxidation of Pu(IV) was observed within first half an hour due to OH generation via Fenton reaction (Figure 15). However, the presence of humic acid significantly inhibited Pu(IV) oxidation, which can be attributed to fast reverse reactions of Pu(V) reduction to Pu(IV) as well as the ·OH trapped by HA.

Concentration distribution of Pu with time shows that Pu mobility decreases with increasing HA concentrations (Figure 16). Before adding H$_2$O$_2$, Pu(IV) formed complexes with HA. Once the reaction started, the percentage of dissolved Pu increased with time at a given HA concentration due to Pu(V) generation. Pu(V) was not complexed with HA at low pH and existed as a dissolved species. With the oxidation to Fe(III), Pu(IV) forms aggregates together with HA and Fe(III). Taken all together, our findings indicate that the HA could inhibit Pu(V) generation and decrease the mobility of Pu during oxidation of anoxic sediments.

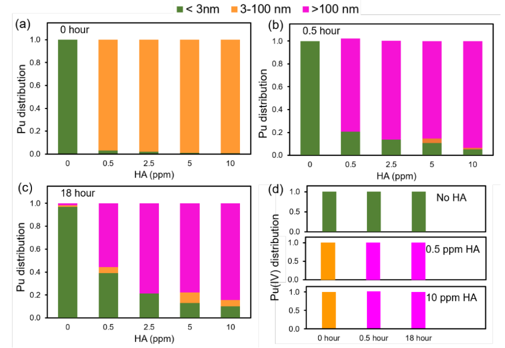


Figure 16. Impact of HA on Pu distribution at different time (a) before H$_2$O$_2$ added (b) at 0.5 hour (c) at 18 hour (d) Pu(IV) distribution.

Focus Area 2C: Microbial influences on actinide stabilization and mobilization

Lead: Y. Jiao, contributors: N. Merino, C. Pan

Hypothesis: *Microbial activity is a key driver of Pu mobility in the environment. The cell surface chemistry and microbial exudate composition affect Pu associations with minerals through aqueous complexation or surface stabilization.*

Microorganisms are known to influence actinide biogeochemical cycling through mechanisms such as bioaccumulation, biosorption, bioreduction, and biomineralization. However, in the context of Pu mobility, little is understood about the microbially-driven processes that influence the environmental fate and transport of Pu. In particular, Pu is known to complex with organic ligands (Figure 17), such as siderophores, citrate, and oxalate (Boukhalfa et al. 2007; Jensen et al. 2011; John et al. 2001), but the direct connection between microbial extracellular products (exudates) and Pu mobility still remains unknown. The overall objective of Focus Area 2C is to understand the influence of microbial exudates on Pu mobility with environmentally relevant microorganisms and metabolisms.

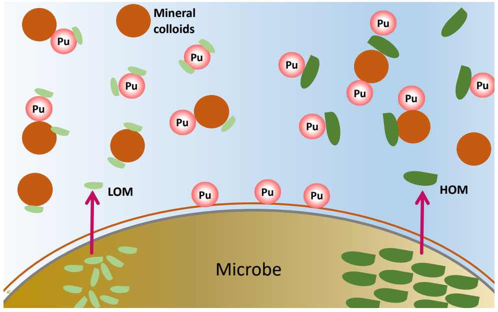


Figure 17. A conceptual model of Pu interaction with LOM (low-molecular weight organic matter) and HOM (high-molecular weight organic matter) fractions of cell exudates that microbes secrete. Various configurations include but are not limited to Pu association with LOM (amino acids, organic acids, sugars), Pu "adsorption" onto HOM (EPS, proteins), Pu-mineral interaction interfaced by OM, or aggregation of Pu associated HOM onto mineral surfaces.

The four tasks associated with this Focus Area include: Task 2C-1: Characterization of microbial exudates and their interaction with Pu, Task 2C-2: Pu mobilization from mineral surfaces by low-molecular weight microbial exudates, Task 2C-3: Pu stabilization by microbial macromolecules on mineral surfaces, and Task 2C-4: Pu incorporation into iron oxides of microbial origin.

In FY19 we started Task 2C-1, the subsequent tasks will start in FY20. Results from these experiments will determine the mechanisms that regulate how microbial exudates complex with Pu, and subsequently affect Pu stability on mineral surfaces or incorporation into secondary minerals. Experiments will be conducted in the context of microbe identity, metabolic functions and pathways, and potentially, specific metabolites. By exploring the relationship between microbial activity and Pu transport (Neu et al., 2005; Panak and Nitsche, 2001; Wildung and Garland, 1982), we will provide mechanistic insights into Pu mobilization and immobilization processes driven by microbial community behavior.

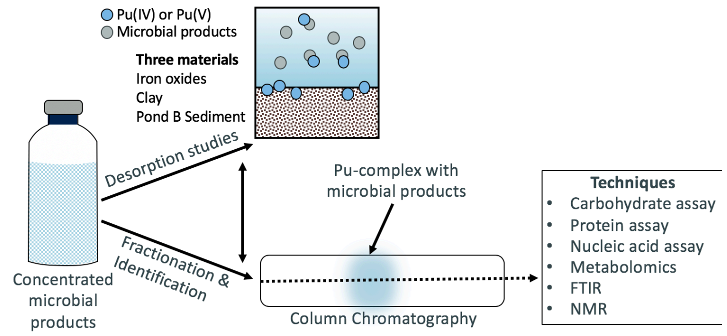


Figure 18. Scheme to examine the influence of intracellular and extracellular microbial exudates on Pu mobility.

Task 2C-1: Characterization of microbial exudates and their interaction with Pu

In FY19, we started a combined field and laboratory experiments to understand the influence of microbial exudates on Pu fate and transport. Water and sediment collected from SRS Pond B in January and June 2019 (Focus Area 1D) are being used to create microcosm experiments to enrich for nine specific metabolisms present in Pond B: photosynthesizers, heterotrophs, iron oxidizers, methanotrophs, purple/green sulfur bacteria, fermenters, iron reducers, methanogens, and sulfate reducers. These correspond to different layers of a stratified pond: epilimnion, thermocline, and hypolimnion (e.g., light/dark cycles, microaerophilic conditions, and anoxic conditions, respectively). The microcosms will be maintained and monitored for 30 days to concentrate the exudates. Subsequently, the microcosms will be processed to focus on (1) intracellular metabolites and extracellular exudates, (2) cell wall and tightly-bound extracellular polymeric substances, and (3) extracellular polymeric substances in biofilms of sediment samples. The cell wall and exudate fractions will be used to probe for Pu and mineral-Pu complexation (Figure 18). Results from these studies will provide much needed insight into the relationship between microbial community composition and metabolisms, the resulting characteristics of extracellular organic matter composition, and impact on Pu fate and transport. In particular, this will enable the development of conceptual models to understand microbial community influence on Pu cycling at SRS Pond B. More broadly, we will begin to build the relationship between geochemical conditions, microbial community dynamics, and radionuclide fate and transport.

4.a.ii Science Highlights

In the following section, we highlight nine publications from June 2018 to June 2019 that summarize the activity of the LLNL SFA. These publications provide the foundation for ongoing investigations into the behavior of actinides at environmentally relevant timescales and across a biogeochemically broad range of field conditions.

Complexation of plutonium(IV) with trans-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic Acid (CDTA) in acidic solution

Fissile U and Pu, which can represent about 97% of the mass of the used nuclear fuel, may be recovered and recycled back into the nuclear fuel cycle and used for further energy production. Additional separations allow for partitioning between the remaining long-lived transuranic elements from the relatively short-lived fission products. Such separations reduce the volume, radiotoxicity, and thermal load of nuclear waste that will eventually be disposed of in a geological repository. Reprocessing of used nuclear fuel is accomplished primarily using liquid–liquid extraction methods. In these systems, complexing agents with an affinity for specific elements are added to improve separation efficiency, as is the case for separation of trivalent actinides from lanthanides. The use of trans-1,2-diaminocyclohexane-N,N,N′,N′-tetraacetic acid (CDTA) has been suggested in the actinide–lanthanide separation and extraction processes to help extract only the targeted actinide elements (Figure 19). LLNL and Washington State University researchers have thus made a study of the interaction of Pu(IV) oxide—PuO_2—with CDTA to better understand and predict used nuclear fuel separation efficiency. *The results and methodology will be applied to the study of Pu mobilization at the Hanford site (Focus Area 1A).*

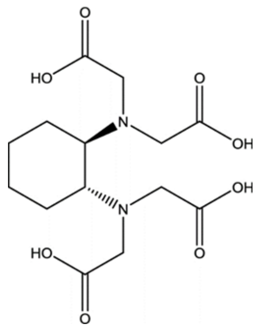


Figure 19. Chemical structure of CDTA

Friend, M.T., Zhao, P., Zavarin, M., and Wall, N.A. 2019. Complexation of Plutonium(IV) with trans-1,2-Diaminocyclohexane-N,N,N′,N′-tetraacetic Acid (CDTA) in Acidic Solution, *Journal of Solution Chemistry* **4** (2), 212–233, doi: 10.1007/s10953-019-00859-1.

Sorption kinetics of plutonium (V)/(VI) to three montmorillonite clays

Previous work has indicated that Pu(V) can be reduced on the surface of minerals, a process that could enhance the uptake of Pu with implications for the mobility of Pu in the environment. In this work, the role of structural Fe in clays on this reduction reaction was investigated by studying Pu sorption rates to three montmorillonite clays with variable Fe content. The clays used were SWy-1 montmorillonite (2.6 wt % Fe), STx-1 montmorillonite (0.6 wt % Fe), and Barasym synthetic mica-montmorillonite (0.01 wt % Fe). The results indicate that at circumneutral pH, structural Fe will affect the kinetics of Pu surface mediated reduction on montmorillonite clays but not necessarily the equilibrium Pu sorption affinity at environmentally relevant timescales (Figure

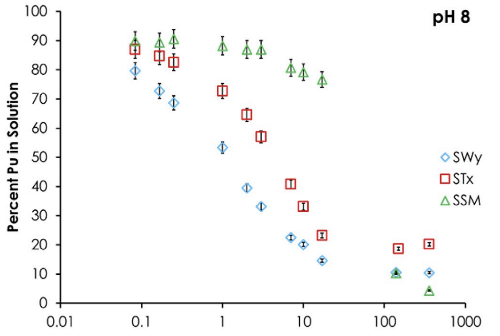


Figure 20. Pu(V) sorption rates to three montmorillonite clays reveals the importance of structural iron on surface mediated Pu(V) reduction kinetics.

20). The differences in rates on the three clays emphasize the need to perform long-term sorption experiments (> 1 year) to adequately capture the equilibrium processes controlling the uptake of Pu especially under atmospheric conditions. Comparison to other minerals indicates that the sorption rates can vary by as much as five orders of magnitude depending on the structure and composition of the surface, highlighting the confounding effect of Pu redox transformation kinetics on its observed behavior and the difficulties this causes for determining equilibrium sorption values. *The work applies to the follow-on studies examining the redox processes that impact Pu fate and transport (Focus Area 1B and 2B).*

Begg, J.D., Edelman, C., Zavarin, M., Kersting, A.B. 2018. Sorption kinetics of plutonium (V)/(VI) to three montmorillonite clays. Applied Geochemistry, 96, 131-137.

Hydrothermal alteration of nuclear melt glass, colloid formation, and plutonium mobilization at the Nevada National Security Site, USA

Approximately 2.8 metric tons of plutonium (Pu) has been deposited in the Nevada National Security Site (NNSS) subsurface as a result of underground nuclear testing. Most of this Pu is sequestered in nuclear melt glass. However, Pu migration has been observed and attributed to colloid facilitated transport. To identify the mechanisms controlling Pu mobilization, long-term (~3 year) laboratory nuclear melt glass alteration experiments were performed at 25 to 200 °C to mimic hydrothermal conditions in the vicinity of underground nuclear tests (Figure 21). At 200 °C, maximum Pu and colloid concentrations of 30 Bq/L and 150 mg/L, respectively, were observed. However, much lower Pu and colloid concentrations were observed at 25 and 80 °C. These data suggest that Pu concentrations above the drinking water Maximum Contaminant Levels (0.56 Bq/L) may exist during early hydrothermal conditions in the vicinity of underground nuclear tests. However, formation of colloid-associated Pu will tend to decrease with time as nuclear test cavity temperatures decrease. Furthermore, median colloid concentrations in NNSS groundwater (1.8 mg/L) suggest that the high colloid and Pu concentrations observed in our 140 and 200 °C experiments are unlikely to persist in downgradient NNSS groundwater. *The work is the result of our longstanding research of colloid-facilitated Pu transport at the NNSS the results will be applied to the efforts planned in Focus Area 1C.*

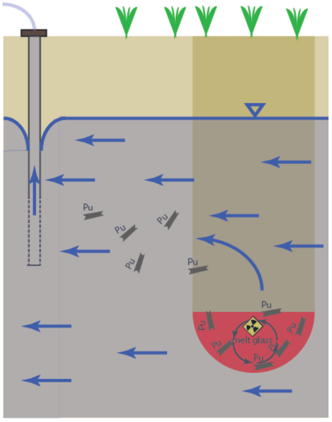


Figure 21. Long-term hydrothermal experiments reveal both the source and the long-term risk of Pu groundwater contamination.

Zavarin, M., Zhao, P., Joseph, C., Begg, J.D., Boggs, M.A., Dai, Z., and Kersting, A.B. Just Accepted. Hydrothermal alteration of nuclear melt glass, colloid formation, and plutonium mobilization at the Nevada National Security Site, U.S.A., Environmental Science & Technology, http://dx.doi.org/10.1021/acs.est.8b07199.

Plutonium desorption from nuclear melt glass-derived colloids and implications for migration at the Nevada National Security Site, USA

The migration of low levels of Pu has been observed at the Nevada National Security Site (NNSS) and attributed to colloids. To better understand the mechanism(s) of colloid-facilitated transport at this site, we preformed flow cell desorption experiments with mineral colloid suspensions produced by hydrothermal alteration of NNSS nuclear melt glass. Three different colloid suspensions were used, 1) colloidal material from hydrothermal alteration of nuclear melt glass at 140°C, 2) at 200°C, and 3) Pu sorbed to SWy-1 montmorillonite at room temperature. The 140°C sample contained only montmorillonite while zeolite and other phases were present in the 200°C sample (Figure 22). The desorption rates for the 140°C colloids and the Pu-montmorillonite colloids were similar. However, the desorption rates from the 200°C colloids were up to an order of magnitude lower. We posit that the formation of zeolites and more crystalline clays at 200°C may lead to a more stable association of Pu with the colloids, resulting in lower desorption rates. This may give rise to more extensive colloid-facilitated transport and help explain why trace levels of plutonium are found downgradient from their original source decades after a nuclear detonation. Interestingly, in the case of cesium (a co-contaminant of Pu), no difference was observed between the 140 and 200°C colloids. This suggests that the Cs sorption mechanism (cation exchange) is not similarly affected. *The work is the result of our longstanding research of colloid-facilitated Pu transport at the NNSS the results will be applied to the efforts planned in Focus Area 1C.*

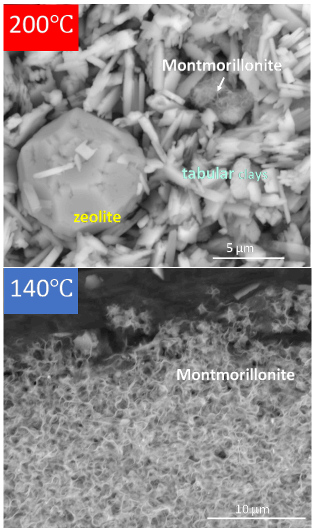


Figure 22. The nature of hydrothermally altered colloids affects the stability of Pu and its migration potential at the NNSS.

Joseph, C., Balboni, E., Baumer, T., Treinen, K., Kersting, A.B., and Zavarin, M. *Submitted*. Plutonium desorption from nuclear melt glass-derived colloids and implications for migration at the Nevada National Security Site, USA, Environmental Science & Technology.

Reduction of Plutonium(VI) to (V) by Hydroxamate Compounds at Environmentally Relevant pH

We examined the reactions of Pu(VI) and Pu(V) with AHA and compared them to reactions with a tri-hydroxamate siderophore, desferrioxamine B (DFOB) at environmentally relevant pH (5.5-8.2). Gas chromatography-mass spectrometry (GC-MS) and UV-Vis spectrometry were combined to track Pu reduction and hydroxamate oxidation. Pu(VI) was instantaneously reduced to Pu(V) (Figure 23). However, further reduction to Pu(IV) did not occur. Similar results were observed using DFOB. These results suggest that the reduction of Pu(VI) to Pu(V) by AHA and DFOB is facilitated by direct one electron transfer. Further reduction to Pu(IV) did not occur because Pu(V) does not form a strong complex with hydroxamate compounds at circum-neutral pH. Broadly, this suggests that Pu(V) reduction to Pu(IV) in the presence of NOM is not facilitated by hydroxamate functional groups and that other natural organic matter moieties likely play a more prominent role. *The results are directly related to the efforts planned in Focus Areas 1D and 2C.*

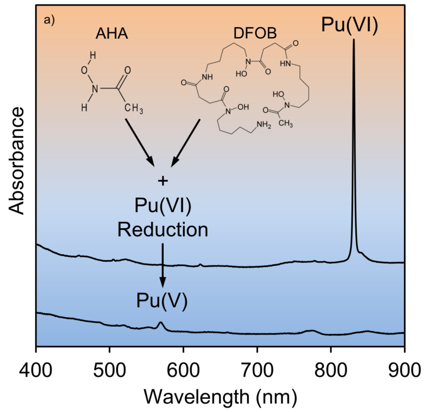


Figure 23. UV-Vis spectrometry reveals the reduction of Pu(VI) to Pu(V) by hydroxamate ligands. However, reduction to Pu(IV) is not observed by this ligand.

Morrison, K.D., Jiao, Y., Kersting, A.B., and Zavarin, M. 2018. Reduction of Plutonium(VI) to (V) by Hydroxamate Compounds at Environmentally Relevant pH, Environ. Sci. Technol., 52:6448–6456.

Thermoanaerosceptrum fracticalcis gen. nov. sp. nov., a novel fumarate-fermenting organism from a deep fractured carbonate aquifer of the US Great Basin

The deep fractured rock ecosystems across most of North America have not been studied extensively. However, the Nevada National Security Site (NNSS, formerly the Nevada Test Site), has hosted a number of influential subsurface investigations over the years. This study focuses on resident microbiota within the fluids from 691 meters below land surface, extracted from monitoring borehole U-3cn#5, which intercepts a hydrogeologically confined aquifer within fractured Paleozoic carbonate rocks. Analysis of the microorganisms living in this oligotrophic environment provides a perspective into microbial metabolic strategies required to endure prolonged hydrogeological isolation deep underground. Here we present a microbiological and physicochemical characterization of this environment and describe a novel bacterial genus isolated from the ecosystem. Strain DRI-13T is a strictly anaerobic, moderately thermophilic, fumarate-respiring member of the phylum Firmicutes (Figure 24). This bacterium grows optimally at 55°C and pH 8.0, can tolerate a concentration of 100 mM NaCl, and appears to obligately metabolize fumarate to acetate and succinate. Culture-independent 16S rRNA gene sequencing indicates a global subsurface distribution, while the closest cultured relatives of DRI-13T are Pelotomaculum thermopropionicum (90.0% similarity) and Desulfotomaculum gibsoniae (88.0% similarity). Strain DRI-13T represents a novel genus of subsurface bacterium isolated from a previously unscreened microbial habitat where geothermally heated water flows through fractured carbonate near an underground nuclear test. *The results are directly related to the efforts planned in Focus Areas 1C and 2C.*

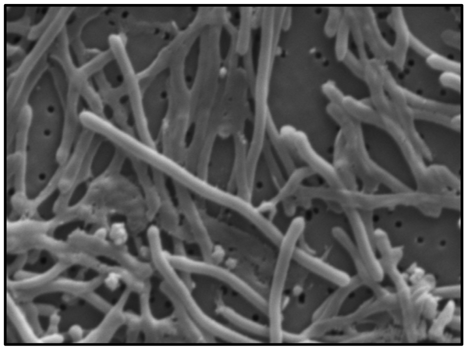


Figure 24. Analysis by scanning electron microscopy (SEM) of isolate DRI-13T revealed a distinctive thin rod-shaped morphology characterized by an average length of 4-6 μm and 0.4 μm width.

Hamilton-Brehm, S.D., Stewart, L.E., Zavarin, M. Caldwell, M., Lawson, P., Onstott, T.C., Grzymski, J., Neveux, I., Sherwood Lollar, B., Russell, C.E., and Moser, D.P. Submitted. Thermoanaerosceptrum fracticalcis gen. nov. sp. nov., a novel fumarate-fermenting organism from a deep fractured carbonate aquifer of the US Great Basin. Frontiers in Microbiology.

Interdisciplinary round-robin test on molecular spectroscopy of the U(VI) acetate system

As a result of the inaugural Advanced Techniques in Actinide Spectroscopy held November 2012 in Dresden GER, LLNL was invited to participate as one of 26 international institutions in a round robin style test of the U(IV) acetate system. The purpose of this test was to evaluate the ability of a range of spectroscopic (vibrational, luminescence, X-ray absorption and NMR spectroscopy) and quantum chemical methods to analyze chemical systems containing actinides. LLNL was tasked with leading 6 of the institutions in the NMR portion of the analytical task. The results of this test assessed the variability of these measurements across the various groups. The multimethodologic approach and the conclusions drawn address not only important aspects of actinide spectroscopy but particularly general aspects of modern molecular analytical chemistry. *The results play in important role in validating the application of LLNL's unique capabilities to this SFA.*

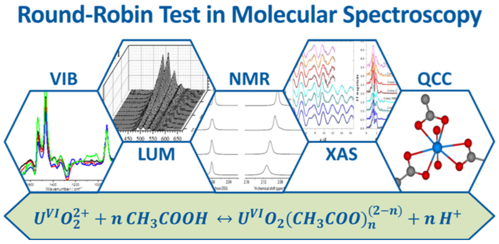


Figure 25. Analytical techniques in the round robin

Müller, K., Foerstendorf, H., Steudtner, R., Tsushima, S., Kumke, M.U., Lefèvre, G., Rothe, J., Mason, H., Szabó, Z., Yang, P., Adam, C.K.R., André, R., Brennenstuhl, K., Chiorescu, I., Cho, H.M., Creff, G., Coppin, F., Dardenne, K., Den Auwer, C., Drobot, B., Eidner, S., Hess, N.J., Kaden, P., Kremleva, A., Kretzschmar, J., Krüger, S., Platts, J.A., Panak, P.J., Polly, R., Powell, B.A., Rabung, T., Redon, R., Reiller, P.E., Rösch, N., Rossberg, A., Scheinost, A.C., Schimmelpfennig, B., Schreckenbach, G., Skerencak-Frech, A., Sladkov, V., Lorenzo Solari, P., Wang, Z., Washton, N.M., and Zhang, X. 2019. Interdisciplinary Round-Robin Test on Molecular Spectroscopy of the U(VI) Acetate System, ACS Omega 2019, 4, 8167–8177.

Environmental chemistry of plutonium

In collaboration with the Karlsruhe Institute of Technology (GER) and the Norwegian University of Life Sciences, we summarize the scientific community's understanding of the environmental chemistry of Pu (Chapter 19 of the Plutonium Handbook) (Figure 26). Fifty years after publication of the original Plutonium Handbook, a timely and authoritative 2nd edition provides unparalleled coverage of plutonium research. Topics span the history of the discovery of Pu, properties of Pu isotopes, chemistry and properties of Pu metal and alloys, Pu aging, thermodynamic trends of Pu, Pu in nuclear fuels, waste forms, and heat sources, packaging, storing, and transportation of Pu, nuclear security and safeguards, and techniques for working with Pu. With authorship from eleven countries, this international collaboration brings together an entire community of researchers from academia, national laboratories, and research institutions. *This work is an outgrowth of LLNL's SFA and the leadership role the program plays in environmental radiochemistry research.*

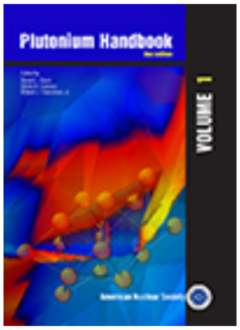


Figure 26. Book cover.

Geckeis, H., Zavarin, M., Salbu, B., Christian Lind, O., Skipperud, L. 2019. Chapter 19: Environmental chemistry of plutonium, *In* Plutonium Handbook, American Nuclear Society.

Radionuclide transport in brackish water through chalk fractures

As radioactive waste produced by the nuclear industry continues to accumulate worldwide, deep geological repositories designed to store high-level waste are being designed and implemented worldwide. In many cases, rock formations investigated as potential sites for repositories contain extensive fracture networks. Fractures have been shown to be strong conduits for water and pollutants in the subsurface, allowing for greater potential mobility of leaked radionuclides. The impact of bentonite colloids on the transport of a cocktail of U(VI), Cs, Ce and Re through fractured chalk was investigated in flow-through experiments using a naturally fractured carbonate rock core (Figure 27). Our results indicate that radionuclide interactions with colloids that undergo flocculation and deposition may effectively immobilize them in brackish aquifers. The results of this study have implications for the prediction of potential mobility of radionuclides in safety assessments for future geological repositories to be located in fractured carbonate rocks in general and in brackish groundwater in particular. *This work was an outgrowth of our SFA and does not directly apply to the LLNL SFA research program. However, it has implications for radionuclide transport in fractured carbonate rock at the NNSS.*

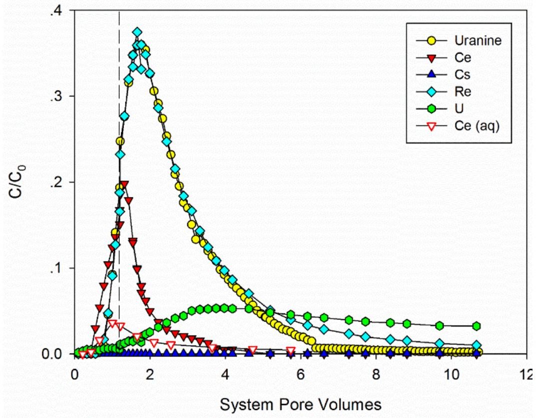


Figure 27. Example breakthrough curve. Dashed line indicates switch from injection of tracer solution to background solution (GW). All concentrations are normalized to the injection concentration. The Ce(aq) species is shown for comparison; however, all other species exhibited no fractionation between the total and aqueous species, indicating that no other metal precipitated as an intrinsic colloid.

Tran, E., Teutsch, N. Klein-BenDavid, O., Kersting, A., Zavarin, M., Weisbrod, N. *Submitted*. Radionuclide transport in brackish water through chalk fractures. Water Research.

4.a.iii Publication Statistics

We continue to target Environmental Science and Technology as the premier journal for environmental science publications (Impact Factor = 7.1). However, our research crosses many fields, from hydrology to basic chemistry, to microbiology (Table 7). Thus, the results of our research have been published across a broad range of journals. To reach a wide audience and maintain LLNL's leadership role in environmental radiochemistry, we are focused on maintaining a presence across a large number of publications.

Table 7. Publication statistics

Journal	Publications	Impact Factor
Water Research	1*	7.9
Environmental Science & Tech	3*	7.1
Frontiers in Microbiology	1*	4.3
Applied Geochemistry	1	2.9
ACS Omega	1	2.6
Journal of Solution Chemistry	1	1.4
ANS book chapter	1	NA

* Including submitted manuscripts

4.b Future Scientific Goals, Vision and Plans

The mission of LLNL's Biogeochemistry of Actinides SFA is to: *Identify the dominant biogeochemical processes and the underlying mechanisms that control actinide transport (focusing on Pu and Np) in an effort to reliably predict and control the cycling and migration of actinides in the environment.*

Our strategic goal is to use our new knowledge gained from this Science Plan to advance our understanding of the behavior of actinides, providing DOE with the scientific basis for remediation and long-term stewardship of DOE's legacy sites and, more broadly, increasing our understanding of transport phenomena in environmental systems sciences with a particular emphasis on **environmentally relevant (long-term) timescales**.

In our 2018 SFA renewal, we shifted the focus of our program to better align with the watershed science goals of the DOE SBR research portfolio and strategic plan. Thus, our research has begun to shift towards a field-oriented research program. We have taken that approach across all the focus areas of our SFA and are focusing our research on environmentally relevant (e.g., decadal) timescales and associated processes. This shift in focus will better allow our SFA to identify processes that would otherwise be missed in more typical short-term experimental time frames. The broad vision for our LLNL SFA is to be a hub for world-class, U.S., and international environmental radiochemistry research and education.

4.c New Scientific Results—*See Section 4.a.ii*

4.d Collaborative Research Activities

We have two subcontracts. One subcontract is with Dr. Brian Powell, Clemson University, SC ($100K/yr). He leads Thrust 1: Focus Area 1E: SRS Radflex facility long-term actinide migration experiment. He co-leads Focus Area 1D: SRS pond B radionuclide cycling between sediments and surface water.

A second subcontract is with Dr. C. Booth at Lawrence Berkeley National Laboratory ($85K/yr). This subcontract supports a postdoc at 0.5 FTE. The subcontract provides our SFA the needed expertise in synchrotron-based actinide spectroscopy that is essential to Focus Areas 1A, 2A, and 2B.

In addition to the funded collaborators, several groups are participating as unfunded collaborators. Dr. Gareth Law (U. of Helsinki and previously at Manchester University) has experience studying the Ravenglass site and is providing guidance in our efforts at that site. D. Kaplan (Savannah River Nat. Lab) has deep insight into the history of Pond B and is providing support with coordinating field work at that site. H. Geckeis, F. Quinto (Karlsruhe Inst. of Tech) are involved in our effort to develop new AMS capabilities at LLNL and are being supported through LLNL's Seaborg Institute. N. Wall (Washington State) and her graduate students (I. Neil and Emily Maulden) are funded through an DOE-EM radiochemistry traineeship consortium and are supporting our efforts at the Hanford site. C. Pierce (Pacific Northwest Nat. Lab.) is supported through PNNL's environmental management program (Vickie Freedman) and providing guidance for our efforts at the Hanford site.

5. STAFFING AND BUDGET SUMMARY

5.a Funding Allocation by Program Element

5.a.i Present Funding

In FY19 our SFA budget was $1.1M. LLNL staff effort and estimated total costs for FY19 are detailed Table 8. We also identify costs based on Focus Areas.

Table 8. Cost breakdown for staff and Focus Areas.

Focus Area	Costs ($K)	LLNL Researcher	Effort (%)	Cost ($K)
1A	200	Annie Kersting	5	32
1B	140	Mavrik Zavarin	19	90
1C	10	Yongqin Jiao	11	49
1D	220[a]	Enrica Balboni[b]	25	70
1E	70[a]	Nancy Merino[b]	54	94
2A	140[a]	Harris Mason	3	11
2B	200	Chao Pan[b]	85	173
2C	120	Keith Morrison[b]	1	5
		Stefan Hellebrandt[b]	75	165
Total	**1.1M**[c]	Administrator	11	22
		Other		33
		Total	**289**[d]	**741**[d]

[a] Includes costs of subcontracts to Clemson (100K) and Lawrence Berkeley National Laboratory (85K).

[b] Note: LLNL postdocs are provided 0.25 FTE funding by LLNL for career development. Costs associated with recently hired postdoc Gauthier Deblonde is not captured in this budget.

[c] Travel is estimated at 15K and procurements at 124K.

[d] Effort does not include postdocs at Clemson and Lawrence Berkeley National Laboratory.

5.b Funding for External Collaborators

See 4.d for details.

5.c Personnel Actions

We converted two postdoctoral fellows to staff positions (Keith Morrison and Enrica Balboni). We have hired two additional postdocs, Nancy Merino (February 2019) and Gauthier Deblonde (April, 2019). Several graduate students associated with the LLNL SFA completed their PhDs and took postdoc positions (Nate Conroy is a LANL postdoc, Mitchel Friend is a LANL postdoc, Corey Pilgrim is an INL postdoc, and Chad Durrant is a LLNL postdoc). Melodie Maloubier (postdoc, Clemson University) transitioned to a staff position the French National Center for Scientific Research (CNRS).

In late FY18, Dr. James Begg moved to Spain. Dr. Enrica Balboni has taken over some of his effort. She was converted from post-doc to staff member and is now leading the Ravenglass Focus Area 1D. Dr. Yongqin Jiao has increased her role on the SFA and is now leading the Surface Aging Focus Area 2B.

5.d National Laboratory Investments

LLNL is providing funding to renovate our Seaborg Institute Laboratory where we carry out experiments with higher levels of radioactivity. This renovation will be a complete rebuild of the laboratory as well as upgrades to our high-activity glove box and controlled atmosphere glovebox. In addition to the Seaborg Institute laboratory renovation, an upgrade to our low-level laboratory is also being pursued.

LLNL continues to support the Seaborg Institutes and its various outreach, internship, and visiting scientist programs. The LLNL SFA is able to take advantage of this support to develop collaborations with a number of national and international institutions (seven total) and host graduate students interested in LLNL SFA research.

5.e Capital Equipment

We anticipate that development of our field sampling and analysis capabilities will require capital equipment purchases. In FY19, field portable pumps, samplers, CTDs to be deployed at the SRS pond B amounted to ~$50k in equipment purchases. Due to the contaminated nature of the site, it is likely that this equipment will be stored at SRS and not available at our other field sites. As our effort at NNSS E tunnel progresses, we anticipate similar capital equipment costs may be required.

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