Lawrence Livermore National Laboratory

LLNL SFA OBER FY21 Program Management and Performance Report:

BioGeoChemistry at Interfaces

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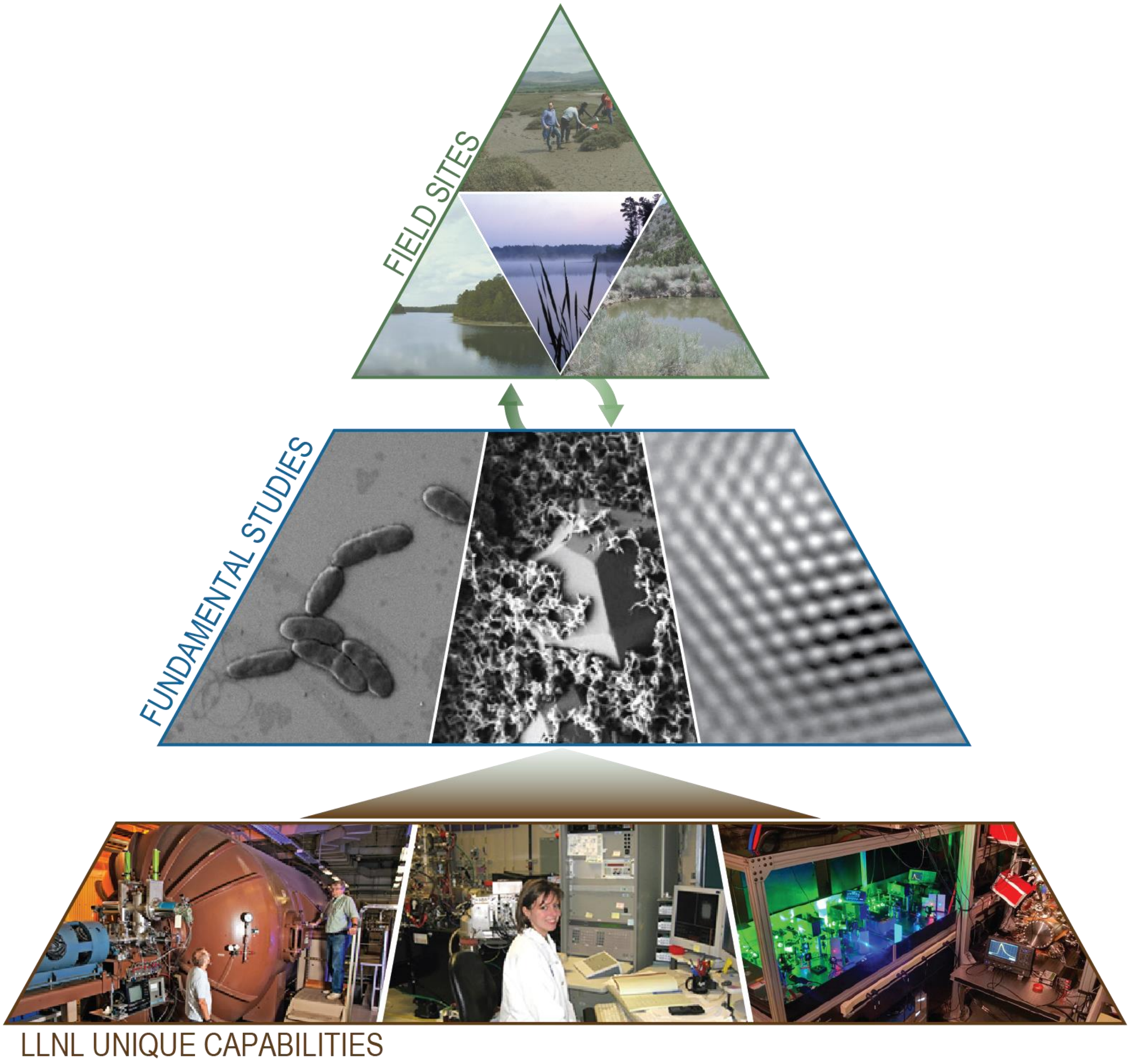


Figure 1. Integration of three core elements in the BioGeoChemistry at Interfaces (formerly BioGeoChemistry of Actinides) Scientific Focus Area.

1. PROGRAM OVERVIEW

The focus of the BioGeoChemistry at Interfaces (formerly 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. These Research Thrusts are underpinned by the unique capabilities and staff expertise at Lawrence Livermore National Laboratory, allowing the *BioGeoChemistry at Interfaces SFA* to advance our understanding of actinide migration behavior in the environment, and serve as an international resource for environmental radiochemistry research (Figure 1). ***Our greater focus on transient redox gradients across stratified waters, sediment-water interfaces, and mineral-water interfaces has led to a reorganization of our SFA to BioGeoChemistry at Interfaces, that better reflects the long-term scientific focus of this SFA and extends beyond actinides to address processes controlling cycling of redox-sensitive metals more broadly.*** 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 our Science Plan to advance our understanding of the behavior of actinides, provide DOE with the scientific basis for remediation and long-term stewardship of DOE's legacy sites. More broadly, we will enhance our understanding of transport phenomena in environmental systems sciences with a particular emphasis on environmentally relevant (long-term) timescales. While we retain our focus on actinide biogeochemistry, our increased focus on overall biogeochemical processes occurring at unique Test Bed locations (associated with this SFA) provides fundamental information on abiotic and biotic redox processes that control the cycling of redox sensitive metals under dynamic and transient conditions.

IMPACT OF COVID-19

COVID-19, the associated shelter in place orders, and minimum safe operations at LLNL have impacted this SFA in many instances. On July 30, 2020, we received notification from BER regarding a one-year extension to our SFA as a result of COVID-19. This additional year with funding at the same level, provides time for the LLNL SFA team to accomplish the original proposed field and laboratory tasks, and maintain appropriate progress and productivity while ensuring the team's safety. This extension has allowed us to address and recover from some of the COVID-19 impacts on our project milestones and deliverables. The impacts of COVID-19 include:

- Reduced access to SSRL. Scheduled beamtime in April was cancelled. SSRL expects to schedule only a fraction of the time originally granted in proposals.
- Delays in a planned mid FY20 start of Focus Area 1C: NTS E-tunnel ponds Test Bed
- Delays in the hiring of two new postdocs
- Delays in analytical chemistry efforts across a number of Focus Area tasks

The changes in performance milestones and objectives (Section 3 of this report) reflect the overall impact of COVID-19 and the associated project delays.

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 FY21, our focus continues to be on plutonium (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 scales, ranging from 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.

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.

As stated earlier, the unique Test Bed locations associated with this SFA are providing fundamental information on redox processes and associated microbiological processes that control the cycling of redox sensitive metals under dynamic and transient biogeochemical conditions. As such, this SFA retains a focus on actinides while expanding its research footprint to metals cycling at interfaces.

3. PROGRAM STRUCTURE

Dr. Felice Lightstone is the Laboratory Research Manager of LLNL's OBER programs. She is group leader in the Biosciences and BioTechnology Division (BBTD) in the Physical and Life Sciences directorate (PLS) and reports on BER activities directly to the Associate Director of PLS, Dr. Glenn Fox. Dr. Mavrik Zavarin is the Director of the Glenn T. 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 together with Dr. Zavarin, oversees 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 2). They co-mentor 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 bi-weekly to present updates, discuss safety, review SFA research accomplishments, goals, and program plans.

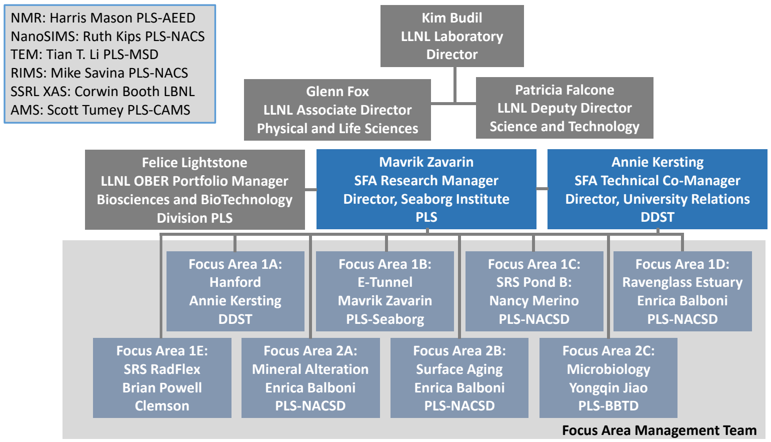


Figure 2. BioGeoChemistry at Interfaces SFA management organization chart.

3.a 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 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 Focus Areas 1B: NTS E Tunnel.

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 helps drive the research agenda with Dr. Zavarin. Together with Dr. Zavarin, she co-mentors the SFA postdocs and graduate students. She leads Thrust 2 and Focus Area 1A: Hanford Z-9 trench.

Yongqin Jiao—Deputy Division Leader for Science & Technology in the Biology and BioTechnology Division at LLNL; 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 postdoc Nancy Merino. She leads Thrust 2 Focus Area 2C: Microbial influences on actinide stabilization and mobilization.

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 Focus Areas 1E: RadFlex facility and co-leads Focus Area 1C: SRS Pond B with Nancy Merino.

Corwin Booth—LBNL staff scientist; a physicist with expertise in strongly correlated f-electron intermetallic and organometallic systems and an expert in applying EXAFS analysis, in particular to transuranic systems. 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.

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 Focus Area 1A: Ravenglass and Focus Areas 2A and 2B (Mineral Alteration and Surface Aging, respectively).

Chao Pan—LLNL postdoctoral fellow. Dr. Pan has a background in aquatic chemistry and environmental geochemistry. Dr. Pan examined the behavior of Pu during Fe(II)/Fe(III) redox cycling and the role of NOM. Dr. Pan recently took a position as Chemistry Lab Director at AEMTEK, Inc.

Nancy Merino—LLNL postdoctoral fellow (started January, 2019). Dr. Merino is a geobiologist with expertise in environmental microbiology, bioremediation, microbe-metal interactions, and bioinformatics. Dr. Merino is co-leading microbial ecology efforts associated with Focus Area 1C: SRS Pond B and is the lead for our data management with ESS-DIVE.

Gauthier Deblonde—LLNL staff scientist recently converted from a postdoc. Dr. Deblonde is a radiochemist with expertise in actinide science, hydrometallurgical processes, ligand-metal interactions, and speciation studies. Dr. Deblonde is studying the interaction of Pu and other actinides with NOM actinide chelators.

Kurt Smith —LBNL post-doc; Environmental radiochemist working for Corwin Booth on XAS spectroscopy (EXAFS / XANES) of actinide systems such as Pu sorption and incorporation into calcite and goethite. Dr. Smith recently took a position as staff scientist at Radioactive Waste Management (UK).

Fanny Coutelot - Clemson University research associate. Dr. Coutelot is a geochemist with expertise in inorganic geochemistry in subsurface waters, transport, and modeling. Dr. Coutelot leads the field sampling effort at SRS Pond B and is examining Pu fluxes at the sediment-water interface.

Teresa Baumer – LLNL postdoctoral fellow (started September 2020). Dr. Baumer has a background in environmental radiochemistry. She is studying the processes controlling Pu migration at the Hanford site for Focus Area 1A: Hanford Z-9 vadose zone actinide migration.

Naomi Wasserman – LLNL postdoctoral fellow (started August 2020). Dr. Wasserman is an isotope geochemist with a focus on redox geochemistry. With this expertise, she is studying Pu and Fe biogeochemistry at SRS (Focus Area 1C), and radionuclide distribution at NNSS (Focus Area 1D).

4. PERFORMANCE MILESTONES AND METRICS

Table 1 shows the planned schedule for each task as identified in the FY20 progress report. Scope was extended into FY22 due to COVID-19 related project delays. The Hanford effort (Task 1A) completion has been delayed to the end of FY22 due to the early departure of postdoc Stefan Hellebrandt. A new postdoc (Teresa Baumer) is now leading the Hanford effort. The Ravenglass effort (Task 1B) has experienced COVID-19 mass spectrometry delays but will be completed in FY21. The E-Tunnel effort was delayed due to travel restrictions. Our first field sampling campaign was successfully completed in April 2021. The field sampling campaign at SRS Pond B was not impacted significantly by COVID-19. However, microbial microcosm experiments experienced delays. Importantly, the two postdocs hired in FY21 will help to reduce any further COVID-related delays.

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				FY22			
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						🟩	🟩	🟦	🟦	🟦	🟦	🟦	🟪	🟪	🟪	🟪 a
	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			🟦	🟦 *							🟦	🟩		🟪	🟪 *	
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.

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

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

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 and Ames, 1975). However, a small fraction migrated deep into the subsurface

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

vadose zone to depths of 37 m. A correlation between Pu and organic components was found in some cases (Cantrell and Riley, 2008), as well as correlation with Fe and P (Buck, 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 and Riley, 2008).

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 (Task 1A-1 and 1A-2) were initiated in FY19 and near completion. Task 1A-3, Pu reprocessing waste reactive transport through sediments, builds on the data obtained in Task 1A-1 and 1A-2. It began in FY20 but delayed due to staffing issues; this effort continues in FY21.

Task 1A-1: Pu complexation with reprocessing waste

The majority of the work for Task 1A-1 was reported in FY20. This task focuses on identifying which components of the waste stream have an influence on Pu migration. Tri -*n*-butyl- phosphate (TBP)is an organic solvent that was used to sequester Pu from the aqueous phase into the organic phase. In an effort to evaluate the influence of TBP on Pu migration behavior, we carried out a series of binary batch experiments between an aqueous phase and organic phase as a function of pH (2 to 8). In the absence of TBP, Pu remained in the aqueous phase across the entire pH range. In the presence of TBP (15%) and nitrate (5M), a significant amount of Pu was sequestered into the organic phase at pH 2 and 3, decreasing with increasing pH. Importantly, these results indicate that Pu may be mobilized into the aqueous phase during infiltration of low ionic strength waters, and has significant implications for the long-term evolution of Pu deposited in the subsurface at Hanford. A draft manuscript summarizing these findings along with the findings of Task 1A-2 and will be submitted in late FY21.

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. We received 15 uncontaminated sediment samples from the soil library at Pacific Northwest National Lab (PNNL) representing the major geologic units beneath the Z-9 trench. We characterized the sediments using X-ray diffraction (XRD) and determined the sediments are primarily composed of quartz, albite, and clay minerals. The buffering capacities of the sediments were determined using acid titration. These findings will be used to inform the design of the column experiments in Task 1A-3.

Pu interactions with the sediments were investigated using batch experiments. In these experiments, trace Pu was mixed in solution with 2 g/L sediment and the solutions were adjusted to pH 2. The batch experiments were sampled over time and the fraction of Pu associated with the sediment was determined. Even at low pH, 60-85% of the Pu sorbs to the sediments within the first 48 hours. This is an important finding for understanding Pu migration beneath the trench because it suggests that the majority of Pu will sorb to the sediments even before acid neutralization of the waste solutions occurs in the subsurface.

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

This task focuses on understanding the reactive transport of Pu through native Hanford sediments using column experiments and simulated Z-9 trench reprocessing waste solutions. We have designed a set of column experiments to elucidate the major mechanisms controlling long-term migration. Based on the buffering capacities determined in Task 1A-2, a series of columns will be set up for each geological of sediment unit. Three different column experiments will be performed. In the first set of experiments, Pu will be loaded onto the column in a 5 M $NaNO_3$ solution at pH 2.5 in the absence of an organic phase. In the second set of column experiments, the Pu will be loaded onto the column in a 5 M $NaNO_3$ solution at pH 2.5 followed by a Pu-free 15% TBP in dodecane. In the third set of experiments, Pu will be loaded onto the column in a 15% TBP in dodecane solution. For all experiments, Pu breakthrough curves will be determined and the dissolved ions, pH, and Eh monitored. At the end of the experiments, the sediment will be removed from the column and characterized by XRD and compared to the unaltered sediment to understand the evolution of the sediments when exposed to the simulated waste components. The sections will then be dissolved and analyzed for Pu to understand the location and migration of Pu through the column. These experiments will give important insight into the role of organics on Pu migration in the vadose zone beneath the Z-9 trench. Our collaboration with staff scientists at PNNL continues and focuses on characterization of contaminated surface sediments at the Z-9 trench which will further help explain the long-term evolution of contamination in a vadose zone environment.

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

Lead: E. Balboni, contributors: G. Law, S. Tumey, and N. Merino

The Sellafield site on the north west coast of England was originally established in 1947 to support the UK nuclear weapons program (Figure 3). 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 (Geckeis et al., 2019). In the Eastern Irish Sea, the majority of the transuranic activity has settled into an area of sediments ("Mud Patch") off the Cumbrian coast (Figure 3). 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).

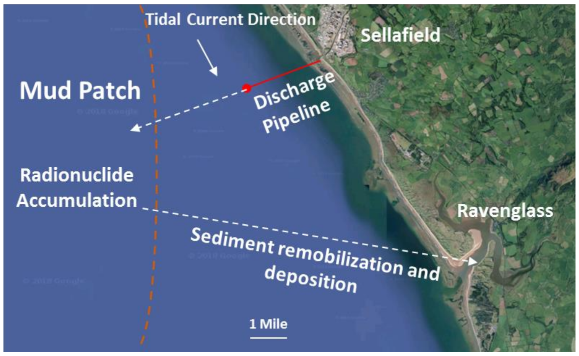


Figure 3. Location of the Sellafield site, mud patch, and Ravenglass Estuary (McCartney et al., 1994; Reynaud and Dalrymple, 2012)

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). 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). Changing redox profiles together with changing hydrological regimes have the potential to impact the speciation and mobility of the redox active radionuclides, including Pu. There are 2 tasks in Focus Area 1B that were part of our efforts beginning in 2017. These Tasks will be completed in FY21.

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

The sediment core collected from the Ravenglass saltmarsh in 2017 is 30 cm in length and was shipped to LLNL where it has been stored under controlled conditions. It was divided in six, 5 cm layers and used to determine the vertical distribution of radionuclides (Pu, Am and Cs) in the sediment column. In the sediment core, Pu reaches a maximum concentration at 10-15 cm (Figure 4) and drops significantly below 15 cm. By matching the Pu profile maxima for ^{239,240}Pu in the sediment core with reported annual discharge peaks (Figure 4), we estimated an average sedimentation rate of 0.4 cm/yr, which agrees with sedimentation rates reported in the area (Morris et al., 2000). The ^{241}Am and ^{137}Cs content was determined via gamma spectroscopy. The peak activity (Bq/g) for ^{137}Cs and ^{241}Am is at 5-10 cm depth, which differs from Pu. These differences in radionuclide peak concentrations highlight differences in radionuclide discharge history and potential radionuclide migration within the sediment column. The results are being prepared for publication along with our Task 1B-2 results.

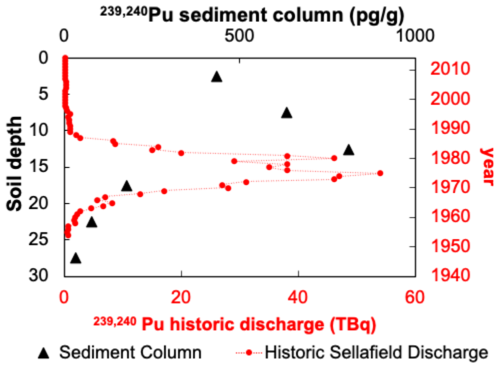


Figure 4 distribution of ^{239,240}Pu in sediment column (black triangles) dated using the Sellafield discharge history (red)

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

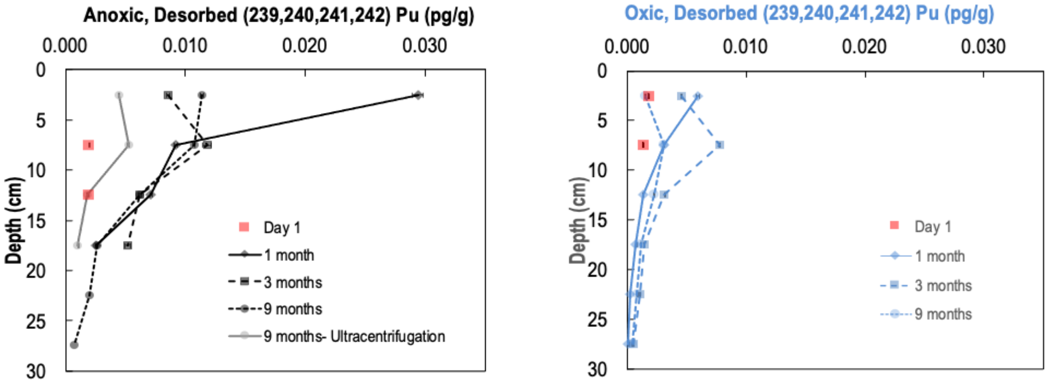


Figure 5 Left: Pu desorption from anoxic (left) and oxic (right) sediments up until 9 months.

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 a nine-month period. The anoxic experiments were conducted in a Coy anaerobic chamber whereas the oxic experiments were started in an anaerobic chamber and subsequently moved to atmospheric condition (bottles capped with porous bungs and shaken periodically). Desorbed Pu (measured by multi-collector inductively couple plasma mass spectrometry) and redox indicators (Eh, pH and extractable Fe(II)) were monitored. In the anoxic experiments, reducing conditions were maintained during the entire sampling period, with Eh ranging between -400 and -200 mV. In the oxic experiments after 1 month the Eh ranged between 300 and 800 mV, indicating that upon exposure to the atmosphere the sediment suspensions became oxidizing. Oxidizing conditions were maintained through the duration of the experiment. Fe(II) was also monitored in these experiments using solid phase chemical extractions that quantify microbially derived Fe(II) and are an indicator of sediment reducing potential (Lovley and Phillips, 1986). In the anoxic experiments, there is a 10-30% increase of Fe(II) in all sediment layers between day 1 to 1 month. After 1 month all of the extractable Fe is present as Fe(II). In contrast, in the oxic experiments the amount of Fe(II) decreases to less 20% after 3 months.

All Pu desorption data have been collected and are reported in Figure 5. Under anoxic conditions and in the top sediment layer layer (0-5 cm) the concentration of desorbed Pu is highest at 1 month and decreases thereafter. However, not much difference in Pu desorption behavior is observed in the deeper sediments. Ultracentrifugation analysis of the 9 month anoxic sample demonstrates that between 50 and 70 % of Pu in these desorption solutions is associated with colloids in the 5-50 nm range. Under oxic conditions less Pu is desorbed from the sediments at every depth compared to the anoxic solutions. Similar to the anoxic experiments however, the most desorption is observed from the top layers of the soil (0-10 cm depth). These findings show that Pu mobilization is enhanced in the shallow sediments and is independent of the Pu concentration in the soil (i.e. Figures 4 vs. 5).

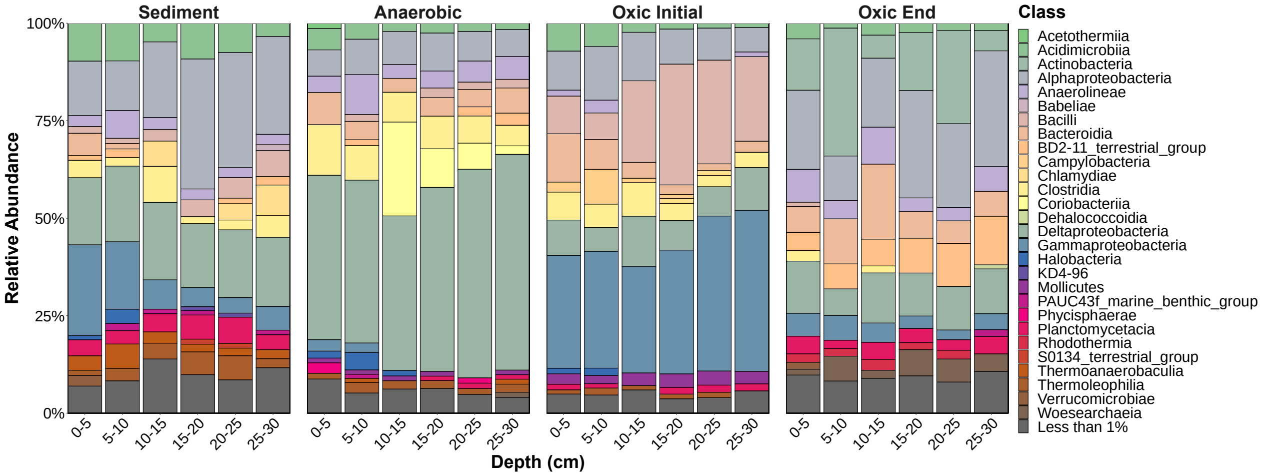


Figure 6. Relative abundances of the microbial community in the sediments.

We have also completed the characterization of the microbial community composition in the sediments (Figure 6). Community variation between the different Sellafield microcosms is largely explained by variations in experimental conditions (oxic vs anoxic) rather than sediment depth. In particular, sediments maintained under anoxic conditions were dominated by sulfate-reducing bacteria (in the Class *Deltaproteobacteria* which includes Orders *Desulfovibrionales*, *Desulfobacterales*, and *Desulfuromonadales*) that have been shown to mobilize or reduce other radionuclides and metals (Abdelouas et al., 2000; Lloyd, 2003; Xu et al., 2017). This suggests that anaerobic biotic processes contributed to the consistently higher Pu mobilization observed in anoxic versus oxic sediments. The results of this work suggest that Pu desorption (and mobilization) increases under anoxic conditions in estuary sediments. This is leading to a paradigm shift in our understanding of Pu redox chemistry and its impact on radionuclide migration. Quantifying the behavior of actinides under such conditions will help to develop predictive conceptual and numerical models of actinide mobility in coastal environments.

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

Lead: M. Zavarin, N. Wasserman (PD); contributors: N. Merino (PD)

The U12E tunnel complex comprises a series of tunnels in Rainier Mesa, Nevada where nine underground nuclear tests were conducted from 1958 to 1977 (Tompson et al., 2011). Continuous discharge from a perched aquifer intersecting the tunnel system drains into a series of eight unlined containment ponds located in an ephemeral stream bed. While radionuclide concentrations in the discharge remain below permissible limits, distribution of contaminants in the pond sediments and shallow groundwater underlying the ponds are unknown. U12E tunnel discharge was directed into the most upstream pond beginning in the early 1960's and has subsequently been re-directed every few years to more downstream ponds as sedimentation obstructs overflow pipes (Huckins-Gang and Townsend, 2014). Inactive ponds are allowed to fully dry during the fall and winter, and pond with water during the spring and summer monsoonal rains. The shallow sediments (~ few meters thick) in the ponds overlie fractured Paleozoic dolomite bedrock which contains the regional aquifer (~465 m depth) (Tompson et al., 2011). The potential for contaminant transport from the ponds to the dolomite aquifer could be greatly affected by fluctuating redox conditions due to seasonal precipitation. In addition, high organic matter from tunnel debris, plant matter, and an accidental oil spill at the mouth of the tunnel, may also influence radionuclide speciation and mobility (Russell et al., 1993).

Focus Area 1C consists of two tasks. The objective of the first task is to assess the radionuclide distribution in the E-tunnel ponds and sediments. This task was started in late FY20 but was subject to field sampling delays due to COVID travel restrictions. The second task, which has not been started, is to examine the role of advective transport in mobilizing contaminants across the pond-sediment interface and into the underlying regional carbonate aquifer.

A manuscript manuscript was recently submitted (see Science Highlights), which examines the groundwater microbial communities of southern Nevada, specifically the Death Valley Regional Flow System (DVRFS). Using network and null model analyses, we determined that the groundwater planktonic microbiome can reflect groundwater flow paths identified by regional groundwater models and may also reveal perturbations to a groundwater basin not captured by hydrogeochemical data alone.

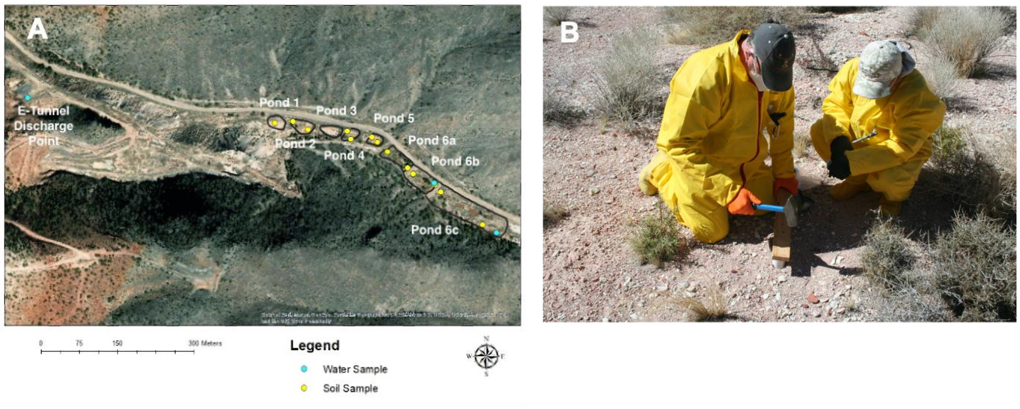


Figure 7. A) Map of sampling water and sediment sampling sites in the E-Tunnel pond system. B) MSTS field technicians collected sediment cores in the E-Tunnel ponds using 6 inch PVC pipe.

Task 1C-1: Characterization of E-Tunnel pond actinide profiles

In collaboration with Mission Support and Test Services, LLC, we conducted the first sampling trip to the E-Tunnel pond system in April 2021 (Figure 7). Thirteen sediment cores (6” deep) were collected from the ponds. Unfiltered water samples were taken from the point of discharge from U12E-tunnel and Ponds 6b and 6c. Due to abnormally dry conditions, only Ponds 6b and 6c, which are actively collecting discharge, contained ponded water. All samples are currently being characterized by gamma spectroscopy and will be subsampled for trace metal analysis, TOC quantification, and XRD in late FY21. Another sampling campaign is planned during wetter conditions to capture contaminant distribution in pond sediments and porewater in a fully saturated state.

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

Lead: B. Powell, N. Merino (PD) contributors: F. Coutelot, N. Wasserman, J. Wheeler, Y. Jiao, K., D. Kaplan

Pond B at Savannah River Site (SRS) is an ideal location for examining the biogeochemical cycling of Pu and other metals. This pond received SRS R reactor cooling water between 1961–1964 containing ^{238,239,240}Pu, ^{137}Cs, ^{90}Sr, ^{241}Am, and ^{244}Cm (Whicker et al., 1990). Since then, Pond B has remained relatively isolated except for a few studies conducted in the late 1980s, which demonstrated Pu cycling with seasonal anoxia (Alberts et al., 1986; Pinder et al., 1992; Whicker et al., 1990). However, the mechanism(s) causing Pu mobilization remain unknown. The objective of Focus Area 1D is to evaluate the concentrations of Fe, Pu, Cs, and organic carbon in Pond B to determine the biogeochemical factors that influence seasonal fluxes in the sediments and overlying pond water.

This Focus Area 1D has two tasks. The focus of the first task (Task 1D-1) is a field sampling program to examine the biogeochemical cycling of Pu and associated redox sensitive metals. 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. The initial phase of Task 1D-1 has been completed and two manuscripts describing the current state of the system in comparison with historical data are in preparation. A second phase of task 1D-2, currently underway, is to examine the heterogeneity of Fe, Pu, Cs, and organic carbon throughout the canal and pond system.

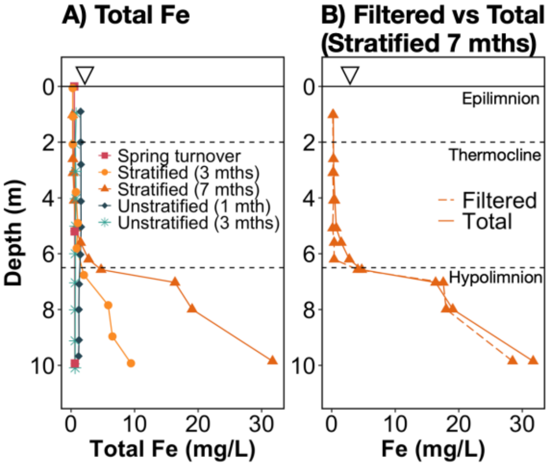


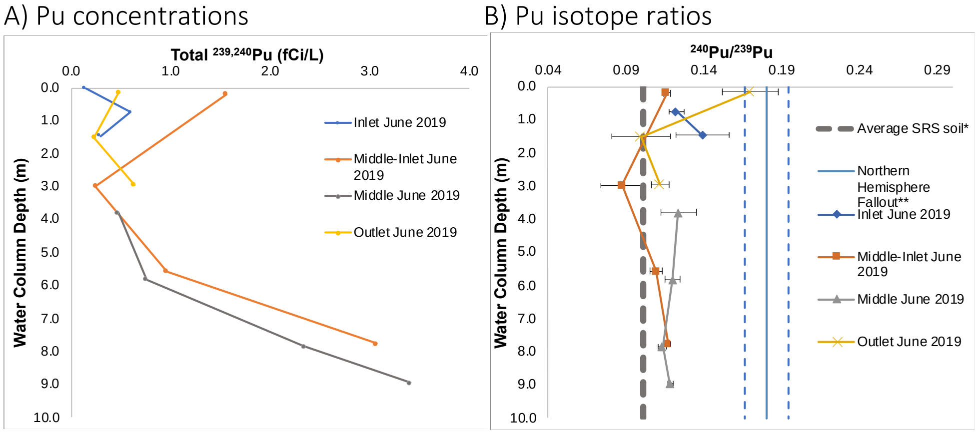
Figure 8. (A) Total Fe over time at the deepest location. Mth = month, or number of months since winter or spring turnover. (B) Total versus filtered (< 0.45µm) Fe.

Task 1D-1: Characterization of Pond B actinide profiles -*Water analyses*

The sampling effort as described in FY20, has been implemented with semi-monthly CTD measurements (i.e., 11 physical parameters) and monthly water column sampling. Four factors exhibit the greatest variation with depth: temperature, oxidation-reduction potential (ORP), total Fe, and TOC. Iron and organic carbon are known to influence Pu behavior. This sampling effort targeted parameters associated with Pu and Cs cycling (e.g., Figure 8A) and includes assessments of total water concentrations (unfiltered column water) and soluble concentrations [filtered; herein, we include the assessment of Fe total (unfiltered) and Fe dissolved (filtered water < 0.45µm) (Figure 8B)]. Fe(II) was measured via a field portable UV-Vis. Preliminary UV-Vis results show a similar profile to the total and dissolved Fe concentrations measured by ICP-MS, as shown in Figure 8B. We identified that an average of about 60–65% of Fe is present as Fe(II) when the water column is not stratified.

Particulate matter composed of organic carbon and iron oxides likely acts as a sorbent material for the complexation of radionuclides and other metals. Previously, we determined that ^{137}Cs concentrations increase with depth, similar to the total Fe concentrations. The majority (about >80%) of the ^{137}Cs was bound to particulate matter (> 900 nm size) (Table 3). We are currently investigating the amount of Pu bound to particulate matter and will be identifying the major components of the particulate matter with depth.

During summer stratification, Pu aqueous concentrations increase with depth, consistent with historical observations (Figure 9A). Iron and ^{137}Cs show similar behaviors, likely a result of reductive dissolution of Fe-(oxy)hydroxides and remobilization of organic matter. These observations are consistent with 1983 measurements of ^{239,240}Pu activity in Pond B, although Pu concentrations have since decreased 2- to 3-fold in the water column. Analysis of March 2020 samples is underway. Pu isotopic ratios (Figure 9B) fall between accepted values for Northern Hemisphere fallout and previously recorded ratios at SRS (Armstrong et al., 2015; Kelley et al., 1999). This range most likely reflects the mixing between atmospheric sources of Pu and historical releases into Pond B from R Reactor.


A) Pu concentrations

B) Pu isotope ratios

Figure 9. (A) Pu concentrations increase with depth due to redox stratification in Pond B. (B) Pu isotope ratios in the water column lie between previously reported SRS values (Armstrong et al., 2015)* and atmospheric fallout (Kelley et al., 1999).**

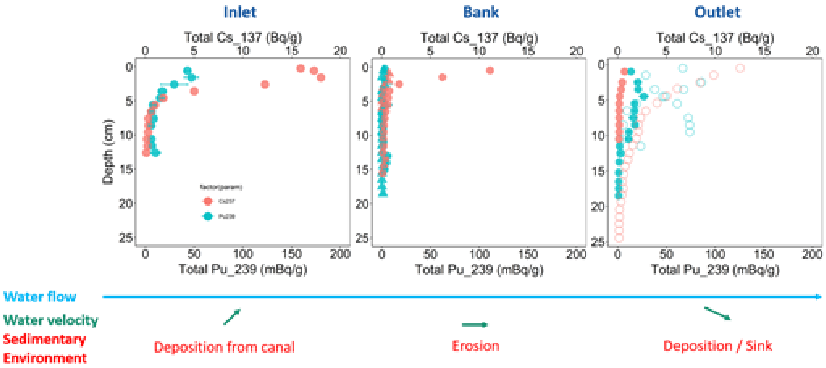


Figure 10: ^{239}Pu (blue) and ^{137}Cs (pink) total concentrations versus depth in sediment cores (solid shapes) collected form the inlet (source), the bank and outlet of pond B the compared the decay corrected cores collected by Whicker et al (1990) at random locations (^{239}Pu and ^{137}Cs open circles).

Task 1D-1: Characterization of Pond B actinide profiles - *Sediment Concentrations*

In July 2019, we collected sediment cores across the pond transect. The cores were then sliced at 1cm intervals and the water, organic matter, total metal and ^{239}Pu content were measured as a function of depth. Comparisons of the concentration profiles within the cores help explain the cycling of these elements within the water column. Total ^{239}Pu and ^{237}Cs from the inlet, the bank and outlet of the pond, show that Pu and Cs accumulation is largely restricted to the upper 5 cm of sediment and decreases with depth for all locations (Figure 10). The inlet (source point) shows the highest levels of Cs and Pu in the pond. The maximum concentrations are lower than those obtained by Whicker et al. (1990).

Table 3. Total versus aqueous ^{137}Cs (Bq/L) from June 2019.

Location, Depth	Total ^{137}Cs	Aqueous ^{137}Cs (< 900 nm size)
Middle, 4.9m	0.18 ± 0.02	0.038 ± 0.027
Middle, 9.9m	0.32 ± 0.01	0.022 ± 0.016
Outlet, 1.5m	0.16 ± 0.02	0.019 ± 0.014
Outlet, 3.0m	0.28 ± 0.03	0.043 ± 0.054

In the Inlet sediment (Figure 11), the upper 5 cm is dominated by Fe and Al. This upper zone is correlated with the production of reduced iron in the pore water, which suggests that Al and Fe (oxy)hydroxides play an important role in scavenging Pu and Cs from the sediments.

Task 1D-2: The role of microbial activity on redox cycling

Previously, we determined that Pond B water microbial community varies with depth rather than location during stratification (Figure 12, stratified ~3 months) and can be categorized by the three distinct stratification layers. The stratified microbiome continues to change throughout the stratification period (Figure 12, compare stratified ~3 and ~7 months data). During spring turnover, the microbiome is similar throughout Pond B (Figure 12, Spring Turnover Avg), reflecting the uniform geochemistry (e.g., oxygen concentrations, temperature, metals). Further analysis of the microbial community is ongoing, including identifying co-occurring microbes and ontological predictions of metabolisms and functions. Future analysis will also include the development of a database of iron oxidizers and reducers for predicting microbial iron redox functions using 16S rRNA amplicon sequencing data.

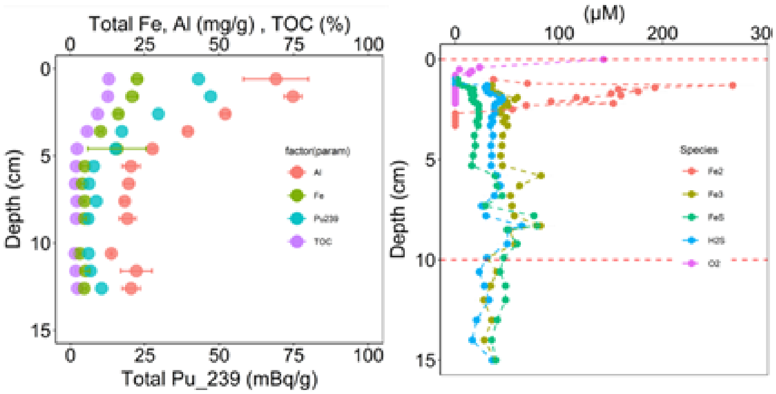


Figure 11: Total solid concentration profile of ^{239}Pu, Iron, Aluminum and Total Organic Carbon in inlet sediment (left). Depth profiles of dissolved oxygen (O_2) (purple), Fe(II) (pink), organic Fe(III)-L complexes (green), ΣH_2S (blue) detected voltammetrically in the inlet sediments. The sediment/water interface is indicated by the horizontal line.

The sediment microbial community was also sequenced from the inlet and outlet locations, and initial results indicate that the inlet microbial community varies within the top 5 cm and remains similar at deeper depths. Since Pu concentrations are highest within the top 5 cm, we will examine potential microbial impacts on redox cycling and Pu mobilization.

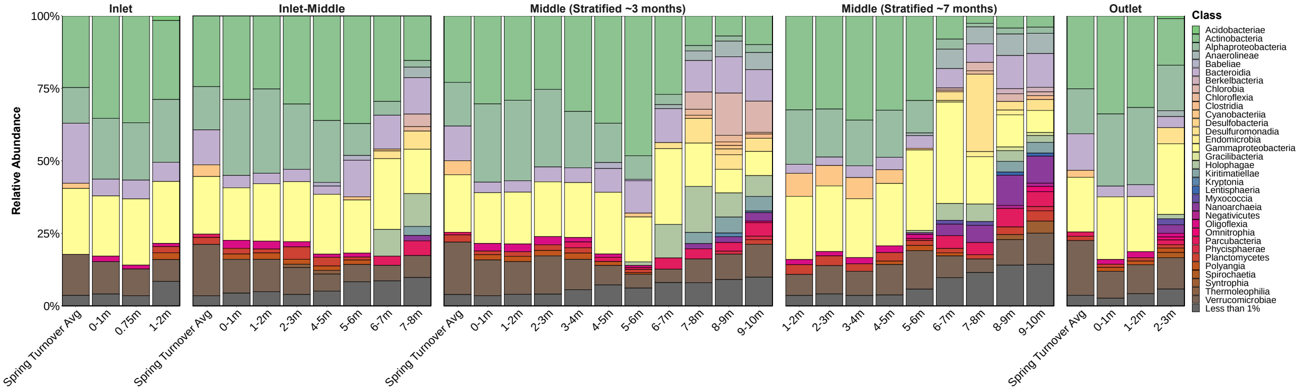


Figure 12. The Pond B microbial community at each location and depth. The middle location was sampled when the pond was stratified for about 3 and 7 months. The community during spring turnover was similar for all depths and was averaged ("Avg").

From the FY20 microbial community results, we developed plans for microcosm studies in FY21 to evaluate the role of iron oxidizers and reducers on metal cycling using iron isotope ratios. Iron isotope ratios could provide valuable information on the biogeochemical transformation and seasonal fluxes of Fe and associated contaminants within Pond B. In particular, partial oxidation and reduction of Fe in the thermocline of the stratified pond may produce isotopically distinct Fe solid phases (Croal et al., 2004; Icopini et al., 2004; Swanner et al., 2017). The magnitude of Fe isotopic fractionation due to microbial reduction and oxidation will be interrogated using microcosms inoculated with anoxic and oxygenated water from Pond B. Changes in the microbial composition, functions, and genes expressed will be examined through metagenomic and transcriptomic analyses, at the Joint Genome Institute through the Biological and Environmental Research Support Science opportunity. We are also collaborating with Dr. Clara Chan (University of Delaware), who is an expert on iron oxidizers and was recently awarded a DOE ESS proposal. Dr. Chan will conduct metagenomic and metatranscriptomic analyses of the water column in the thermocline to identify iron oxidizers and their functions and activity. Taken together with the Fe isotope microcosm studies, we will provide necessary insight into the microbial iron cycle ongoing within Pond B and its impact on metal cycling.

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

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

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 (SRNL) and Dr. Brian Powell (Clemson). 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.

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

Consistent with observations in other research thrusts of this SFA, deployed lysimeters containg $Pu^{V}(NH_4)(CO_3)(s)$ sources have demonstrated the profound importance of natural organic matter on Pu migration. Lysimeters were deployed in FY20 and within 12 months, soluble Pu was already being measured in the lysimeter effluents. It is noteworthy that these effluents have low ORP values and slightly higher pH values than non-organic matter amended lysimeters. In FY22, we will examine if the observed enhanced mobility of Pu is due to changes in pH or complexation with organic matter. Additionally, we plan to remove one set of the triplicate lysimeters containing $Pu^{III}_2(C_2O_4)_3(s)$, $Pu^{V}(NH_4)(CO_3)(s)$, $PuO_2(s)$ and $Pu^{IV}(C_2O_4)_2(s)$ sources which have now been deployed for nearly 9 years. Analysis of these source materials will be compared with our previous FY18 analyses that indicated all Pu sources transformed to a distorted $PuO_{2+x-y}(OH)_{2y}{\cdot}zH_2O$ type structure after 2-4 years. These new data will provide an assessment of the rate of Pu solid phase transformation which influences the release rate of Pu from the source.

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

Thrust 2 Coordinator: A. Kersting

Research Thrust 2 is focused on the processes that may lead to long-term stabilization of actinides in sediments. We focus on three broad categories of stabilization (co-precipitation with 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 process is of central importance to at least one field site being investigated. However, the processes of co-precipitation, surface reactions and microbial interactions are applicable across a wide range of hydrologic conditions beyond the specific field sites of our SFA.

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

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

Knowledge of the interactions of actinide ions with mineral is important for understanding its long-term environmental behavior. Iron (oxy)hydroxides are common soil minerals and are present in intermediate level 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., 2005; 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., 1985b; Zhao et al., 2016) but Fe minerals in dynamic biogeochemical settings will likely be subject to dissolution and recrystallization (e.g. SRS Pond B). Under such a model, incorporation or co-precipitation reactions may offer more meaningful insight into Pu 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 Pu is key in predicting its long-term stability and mobility.

There were two tasks associated with Focus Area 2A. Task 2A-1, initiated in FY19, focuses on Pu coprecipitation with Fe-oxides and calcite, and will be completed in FY21. Task 2A-2 was intended to explore the formation of actinide-Al solution complexes relevant to the Hanford Test Bed Focus Area. It was started in FY19 but was put on hold due to project reprioritization.

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

In FY20/21, we finalized our work describing Pu coprecitpitation processes into oxidized forms of iron oxides (hydrous ferric oxide and goethite). We investigated the fate of Pu during the formation of ferrihydrite and its subsequent recrystallization to goethite. Our results demonstrate that the nature of Pu associated with the precursor ferrihydrite (adsorbed versus coprecipitated) has a direct impact on the behavior of Pu with its recrystallization product goethite. The results provide valuable new insights into Pu(IV)- iron (oxy)hydroxide interactions and highlight the importance of understanding the fate of radionuclides during mineral recrystallization processes. In FY21 we also completed our work aimed at understanding the coprecipitation behaviour of Pu with calcite ($CaCO_3$). Calcite is a common secondary phase in near surface environments and a major component of many rocks and soils. In geological repositories, calcite is expected to form as an alteration product of cement-based materials. The reactivity of the calcite and its ability to tolerate significant variations in its chemical composition through substitution of Ca for other cations make calcite a potentially important sink for environmental contaminants. In our work, single crystals of calcite were synthesized from aqueous solutions containing Pu either as Pu(VI) or Pu(IV) and were characterized using a combination of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and x-ray absorption spectroscopy (XAS). Overall, the LA-ICP-MS and EXAFS data clearly support the coprecipitation of plutonyl in the bulk calcite. These findings suggest that Pu sequestration in calcite may immobilize Pu and isolate it from groundwater interaction in contaminated environments. The results of the calcite work were recently submitted for publication and described in the Science Highlights.

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

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

Although 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 SFA work, we have focused on aging processes in binary actinide-mineral systems (Begg et al., 2014; Begg et al., 2017; Begg et al., 2013; Zhao et al., 2016). In natural environments however, these 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.

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 and 2B-2 were completed in FY21 and a paper describing this work can be found in the Science Highlights. Tasks 2B-3 (Isotopic fractionation of Pu during sorption) was planned for FY20 but was delayed to FY21 due to COVID. We have recently hired a new postdoc (Naomi Wasserman) who has significant expertise in this area and will lead this task. By investigating the way in which Fe redox cycling controls metal mobility, we will gain a better understanding of how actinides behave in dynamic biogeochemical environments.

Task 2B-3: Isotope Fractionation

Similar to other heavy metals, Pu isotopes have the potential to undergo mass-dependent and mass-independent fractionation. Reactions that control actinide mobility, such as adsorption/desorption and redox transformations, are known to fractionate uranium (U) isotopes through the nuclear volume effect (Stirling et al., 2007; Brennecka et al., 2010; Jemison et al., 2016). Previous studies have leveraged U isotope ratios to shed light on U fate and transport in contaminated sites (Brown et al., 2016; Jemison et al., 2020) and comparable applications are also possible for Pu isotopes, which are close to U in mass. In order to characterize Pu isotopic fractionation, we will carry out a series batch sorption experiments with an isotopically characterized Pu standard. Suspensions (0.2 g/L) of high Fe montmorillonite (SWy-2) and Fe-free montmorillonite (Syn-1) in a synthetic groundwater matrix at pH 8.0 will be equilibrated with Pu(IV) (Begg et al., 2018). At various time points prior to isotopic equilibration, the liquid and solid from each reactor will be prepared for Pu isotopic analysis via multi-collector inductively plasma mass spectrometry. Several reactors will also be characterized after isotopic equilibration to track isotopic effects of Pu desorption. Currently, we are determining adsorption coefficients and sorption kinetics using ^{238}Pu. The isotopic fractionation experiments will begin in late FY21.

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

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

Microorganisms are known to influence metal 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. The overall objective of Focus Area 2C is to understand the influence of microbial exudates and cells on Pu mobility with environmentally relevant microorganisms and metabolisms. There are four tasks associated with Focus Area 2C. In FY19–21, we conducted microcosm experiments to collect microbial exudates and cells and test Pu binding affinity to (1) extracellular and intracellular products, (2) the cell wall, and (3) fragmented cell walls. Results from Focus Area 2C 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. We aim to provide mechanistic insights into Pu (im)mobilization processes driven by microbial community behavior, enabling the development of conceptual models to understand the microbial influence on Pu cycling at SRS Pond B. More broadly, we will begin to identify the relationship between geochemical conditions, microbial community dynamics, and radionuclide fate and transport.

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

This task aims to identify microbial exudates that interact with Pu. We expanded this task to encompass intracellular microbial products and the cell wall to understand how microorganisms influence Pu immobilization. We conducted microcosm experiments to enrich for specific metabolisms present in Pond B, as discussed in the FY20 report. Subsequently, we examined the cell exudates (≥1 kD) that complex Pu and observed that the majority of Pu was associated with exudates in the 1-3kD size range, with the exception of exudates derived from algal, methanotrophic, and anoxic sulfate-rich conditions (Figure 13). The Pu was dominantly associated with algal exudates in the 1-10 kD size range and methanotrophic and anoxic sulfate-rich exudates in the >100 kD size. In FY21, the exudates will be characterized using fluorescence spectroscopy to identify the dominant compound families for each size fraction. Similar experiments will also be conducted for the intracellular microbial products in late FY21.

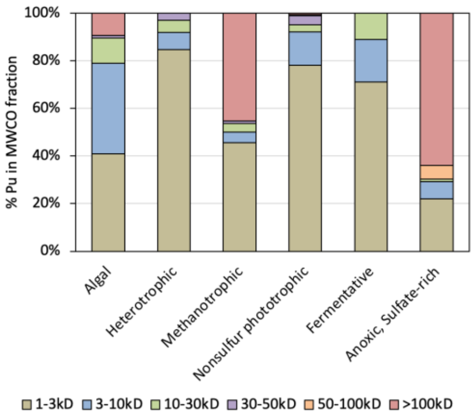


Figure 13. Pu(IV) sorption to exudates by molecular size. MWCO = molecular weight cutoff.

We also examined Pu partitioning to microbial cells in SRS Pond B waters (Figure 14). The cells were added to Pond B water at varying cell concentrations, and we found that the majority of microbial cells required 10^5–10^6 cells/mL to effectively sorb Pu. For comparison, the *in-situ* cell concentrations in Pond B water are about 10^5 cells/mL. The least sorptive cells were those derived from the methanotrophic and algal condition while the most sorptive cells were those from the fermentative condition. The fermentative microbial cells may have cell walls containing tightly-bound extracellular polymeric substances with a high affinity for complexing Pu. These results demonstrate that there is differential Pu sorptive capacity by microbial cells.

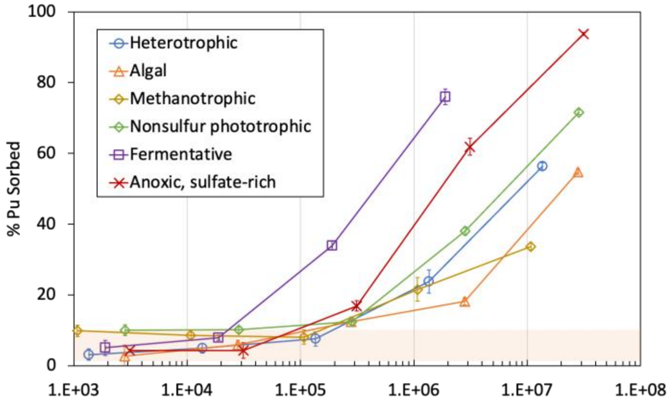


Figure 14. Pu(IV) sorbed to varying cell concentrations. The light orange bar indicates background Pu(IV) sorption.

Tasks 2C-2 AND 2C-3: Pu (im)mobility from mineral surfaces by microbial exudates

Based on observations and results from Task 1D-1 and 2C-1, we planned to setup microcosms representing the sediment-water interface at SRS Pond B. However, due to delays in obtaining the necessary work controls (e.g., HEPA-filter vented anaerobic chamber), we paused the sediment-water interface microcosms. Instead, in FY21, we are utilizing the microbial exudates generated for Task 2C-1 and producing iron oxides, following methods from Task 2A-1. A diffusion cell apparatus, as described in the proposal, will be used for experiments containing the different microbial exudates from Task 2C-1 and iron oxides with Pu sorbed or co-precipitated. The goal of Task 2C-2 and Task 2C-3 is to determine the ability of microbial exudates to mobilize Pu from mineral.

Task 2C-4: Pu incorporation into iron oxides of microbial origin

Task 2C-4 aims to examine the nature of Pu interaction and incorporation into biogenic iron oxides. From observations in Task 1D-1, we determined that iron and organic carbon are two important factors during summer stratification of Pond B. Moreover, microbial community data collected from Task 1D-2 revealed that iron oxidizers and reducers are part of the dominant community. Several of these microbes occupy specific ecological niches within the water column, likely based on the surrounding biogeochemical conditions, such as dissolved oxygen. These ecological niches are sustained throughout stratification (Figure 15).

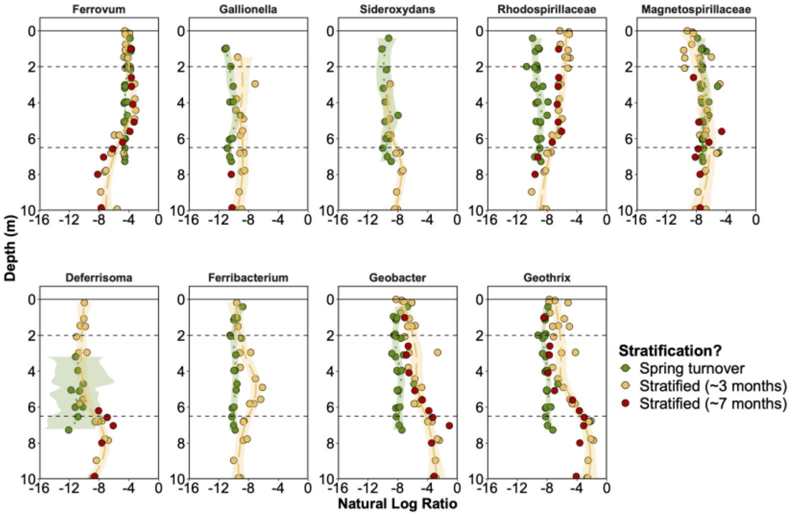


Figure 15. Distribution of putative iron oxidizers and reducers in the Pond B water column. The natural log ratio was determined using Songbird (Morton et al., 2019) and Qurro (Fedarko et al., 2020) as the microbe of interest relative to the whole community. A regression curve using loess smoothing and 95% confidence interval are depicted.

In FY20, microaerophilic and photoferrotrophic iron oxidizers were enriched and subcultured. The photoferrotrophic iron oxidizers were able to oxidize iron for more than 60 days (Figure 16) and produced small, globular iron oxides. The photoferrotrophic culture was dominated by *Rhodomicrobium udaipurense*, *Telmatobacter* sp. BSL-1, and *Bacteroides xylanolyticus* BSL-1. Notably, at least one *Rhodomicrobium* species (*R. vannielii* strain BS-1) is known to oxidize iron (Heising and Schink, 1998). For the microaerophilic iron oxidizers, iron oxides were produced, but the iron oxidation activity diminished over time, likely due to encrustation of cells by iron oxides. Additional growth conditions will be tested for the microaerophilic iron oxidizers in FY21-22 to improve iron oxidation activity. In FY22, we will identify the mineral phases produced by these enrichment cultures, and we will conduct experiments to study the microbial effect on Pu incorporation into Fe minerals. Pu will be introduced at the beginning of iron oxide formation under microaerophilic or photoferrotrophic conditions. A control set of experiments without microbes will be used to identify differences between Pu incorporation into biotic and abiotic formed iron oxides. These data will complement our results from Focus Area 2A, providing relevant information on the influence of microorganisms on Pu incorporation into Fe minerals.

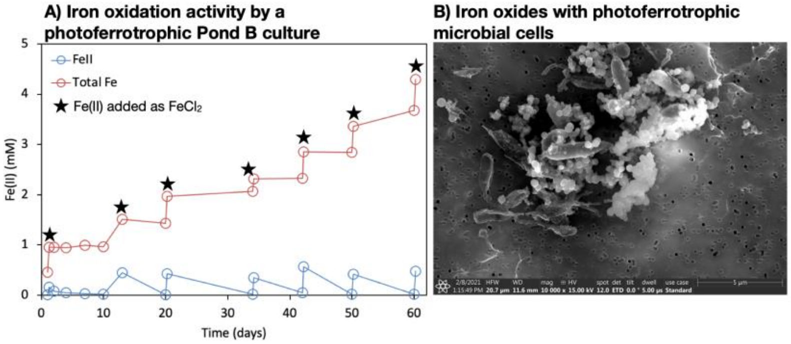


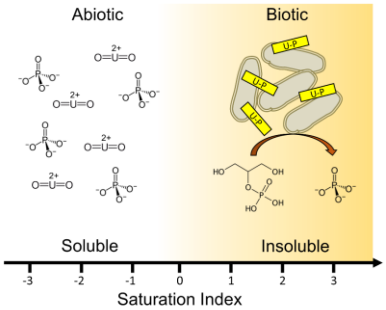
Figure 16. A) Iron oxidation activity by a photoferrotrophic Pond B enrichment culture. Iron oxidation activity was sustained > 60 days. B) SEM image of iron oxides produced by the photoferrotrophic culture (scale bar is 5 µm).

4.a.ii Science Highlights

A total of 10 manuscripts were published or submitted for publication to date as part of this reporting period. Here we highlight 4 of these publications.

It's Only Natural: Using Environmental Microbes to Remove Uranium from Groundwater

Uranium contamination of soils and groundwater in the United States represents a significant health risk and will require multiple remediation approaches. The U.S. EPA has set the drinking water standard for U at 0.03 ppm. Yet, most bioremediation studies are rarely conducted at U concentrations this low.

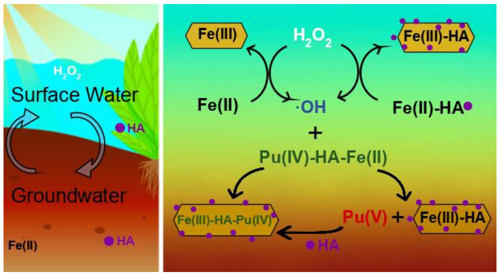


The coupling of microbial enzyme activity and surface adsorption of uranium can lead to the precipitation of highly insoluble U-phosphate minerals that do not precipitate abiotically.

In this study we showed that U-phosphate minerals do not form abiotically in solution when U concentrations are <0.25 ppm and pH is <5, in contrast to previous studies conducted at higher concentrations. Instead, bacteria can facilitate the precipitation of U-phosphate minerals that do not precipitate abiotically. The bacterial surfaces can facilitate the precipitation of U-phosphate minerals by providing a local environment that is supersaturated with respect to U-phosphate minerals, leading to heterogeneous nucleation and mineralization. This microbially mediated process can lower U concentrations below the EPA drinking water limit. These results should be valuable in guiding future microbially based U and phosphate-based remediation strategies where efforts are focused on higher concentrations and pH ranges.

Morrison, K.D., Zavarin, M., Kersting, A.B., Begg, J., Mason, H.E., Balboni, E., & Jiao, Y. (2021) The Influence of Uranium Concentration and pH on U-Phosphate Biomineralization by Caulobacter OR37. Environ. Sci. Technol. 55,3,1626-1636. https://doi.org/10.1021/acs.est.0c05437

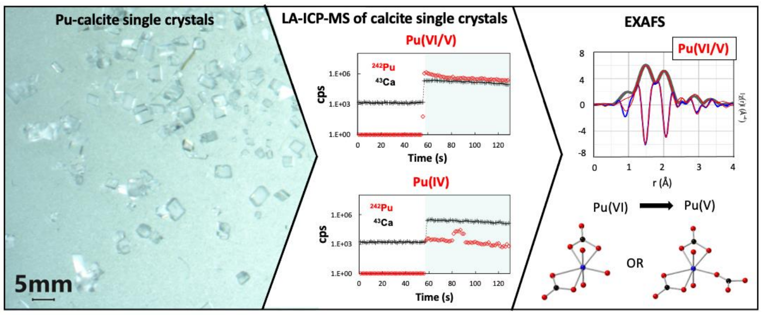
Experiments Reveal Pu Oxidation and Mobilization in Organic Rich Redox Transition Zones



Pu redox and complexation processes in the presence of natural organic matter (NOM) and associated iron can impact the fate and transport of Pu in the environment. To understand Pu in hyporheic zone where surface water and groundwater mixes, we studied the fate of Pu(IV) in the presence of humic acid (HA) and Fe(II) upon reaction with H_2O_2 that may be generated by photochemical reactions in surface water. With the addition of 100 µM H_2O_2, a portion of Pu(IV) was oxidized to Pu(VI/V), which is primarily ascribed to the generation of reactive intermediates from the oxidation of Fe(II) and HA-Fe(II) by H_2O_2. The kinetics of Pu(IV) oxidation at pH 3.5 and pH 6 can be described by a new model that incorporates HA modified Fenton reaction, Pu(IV) oxidation by reactive intermediates, and Pu(VI/V) reduction by HA. Our results reveal H_2O_2 driven oxidation of Pu(IV)-HA-Fe colloids and provide direct evidence for the transient mobilization of Pu in organic rich redox transition zones.

Pan, C., Jiao, Y., Kersting, A.B., & Zavarin, M. (2021). Plutonium Redox Transformation in the Presence of Iron, Organic Matter and Hydroxyl Radicals: Kinetic and Mechanistic Insights. Environ. Sci. Technol. 55,3,1800-1810. https://doi.org/10.1021/acs.est.0c08195.

Plutonium Coprecipitation with Calcite

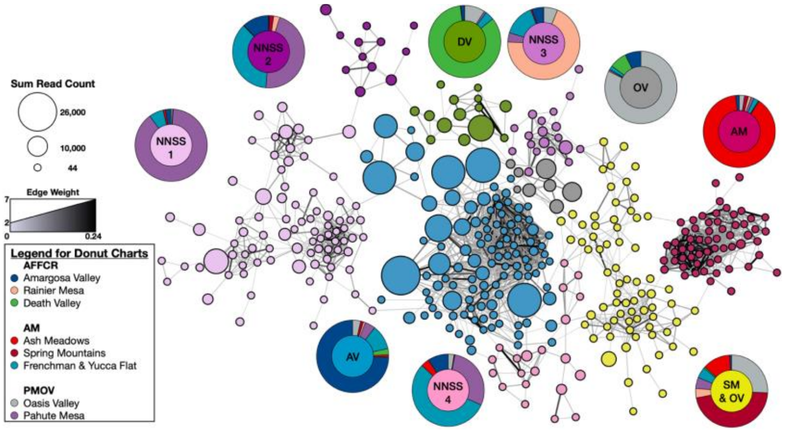


Single crystals of calcite were synthesized with Pu and characterized to determine the amount, structure and oxidation state of coprecipitated Pu.

The mobility of Pu in the subsurface is affected by Pu-mineral interactions such as adsorption-desorption and structural incorporation. In this work, single crystals of calcite were synthesized from aqueous solutions containing Pu either as Pu(VI) or Pu(IV) and characterized using a combination of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and x-ray absorption spectroscopy (XAS). These data were used to assess the amount, structure and oxidation state of Pu coprecipitated into calcite, providing insight into the potential for Pu sequestration in calcite precipitates. Overall, the XAS and LA-ICP-MS data support the coprecipitation of plutonyl (PuVI/V) in the bulk calcite, though the exact nature of the complex is difficult to elucidate. The coprecipitated plutonyl could be either incorporated in distorted Ca lattice sites or in defect sites. We provide evidence to suggest that Pu(VI) is reduced to Pu(V) during calcite synthesis, but no further reduction to Pu(IV) is observed. The LA-ICP-MS additionally shows that the coprecipitation of Pu(VI/V) is favored over the coprecipitation of Pu(IV). Overall our results suggest that Pu sequestration in calcite under environmental conditions could immobilize Pu and isolate it from groundwater interactions in contaminated environments and nuclear waste repositories.

Balboni, E., Smith K.F., Moreau L., Wimpenny J., Booth, C., Kersting A., M. Zavarin <u>*submitted to*</u> *ACS Earth and Space Chemistry (2021)*

Subsurface Planktonic Microbial Communities Reflect Regional-Scale Groundwater Hydraulic Connectivity



Network analysis of the DVRFS planktonic microbial community identified clusters of common microbes that reflected regional groundwater flow paths.

Subsurface microbial communities are impacted by biogeochemical and groundwater fluxes and may inform hydraulic connections. In this study, we examined the regional-scale microbiome of the Death Valley Regional Flow System (DVRFS) to determine whether the groundwater planktonic microbiome reflects flow paths identified by regional groundwater models. Samples were collected from three DVRFS groundwater basins: Pahute Mesa–Oasis Valley (PMOV), Ash Meadows (AM), and Alkali Flat–Furnace Creek Ranch (AFFCR). The diversity within and between communities varied by location. Network analysis revealed patterns between clusters of common microbes that reflected regional flow paths, which were further substantiated by null model analyses for identifying deterministic and stochastic ecological processes that contribute to microbial community assemblages. The DVRFS planktonic microbiome reflected the following flow paths: (1) Spring Mountains to Ash Meadows; (2) Frenchman Flat and Yucca Flat to Amargosa Desert; and (3)

Amargosa Desert to Death Valley. The Pahute Mesa to Oasis Valley flow paths were not supported by microbial community analyses, suggesting that microbial differences could result from slow travel times, groundwater mixing, biogeologic barriers, or underground nuclear tests. This study demonstrates the utility of combining microbial data with hydrogeochemical information to comprehensively characterize groundwater systems for sustainable groundwater management.

Merino, N., Jackson, T.R., Campbell, J.H., Kersting, A.B., Sackett, J., Zavarin, M., Hamilton-Brehm, S.D., Moser, D.P. submitted to PNAS (2021)

Full list of publications

1. Damerow, J.E., Varadharajan, C., Boye, K., Brodie, E.L., Burrus, M., Chadwick, K.D., Crystal- Ornelas, R., Elbashandy, H., Alves, R.J.E., Ely, K.S., Goldman, A.E., Haberman, T., Hendrix, V, Kakalia, Z, Kemner, KM, Kersting, AB, Merino, N, O'Brien, F, Perzan, Z, Robles, E., Sorensen, P., Stegen, J.C., Walls, R.L., Weisenhorn, P., Zavarin, M. and Agarwal, D. (2021). Sample Identifiers and Metadata to Support Data Management and Reuse in Multidisciplinary Ecosystem Sciences. *Data Science Journal*, 20, 11, 1–19. DOI: *https://doi.org/10.5534/dsj-2021-011*
2. Emerson, H.P., Pearce, C.I., Delegard, C.H., Cantrell, K.J., Snyder, M.M.V., Thomas, M.L., Gartman, B.G., Miller, M.D., Resch, C.T., Heald, S.M., Plymale, A.E., Reilly, D.D., Saslow, S.A., Neilson, W., Murphy, S., Zavarin, M., Kersting., A.B., Freedman, V.L., (*2021*). Influences on Subsurface Plutonium and Americium Migration. *ACS Earth Space Chem.5,2,279-294. https://doi.org/10.1021/acsearthspacechem.0c00277*
3. Morrison, K.D., Zavarin, M., Kersting, A.B., Begg, J., Mason, H.E., Balboni, E., & Jiao, Y. *(2021)* The Influence of Uranium Concentration and pH on U-Phosphate Biomineralization by *Caulobacter* OR37. *Environ. Sci. Technol*. 55,3,1626-1636. *https://doi.org/10.1021/acs.est.0c05437*
4. Pan, C., Jiao, Y., Kersting, A.B., & Zavarin, M. *(2021).* Plutonium Redox Transformation in the Presence of Iron, Organic Matter and Hydroxyl Radicals: Kinetic and Mechanistic Insights. *Environ. Sci. Technol*. 55,3,1800-1810. *https://doi.org/10.1021/acs.est.0c08195*
5. Deblonde, G.J.P., Kersting, A.B., & Zavarin, M. (*2020)* Open Questions on the Environmental Chemistry of Radionuclides. *Commun. Chem.* 3, 167-171. *https://doi.org/10.1038/s42004-020-00418-6*
6. Balboni, E., Smith, K.F., Moreau, L., Li, T.T., Maloubier, M., Booth, C., Kersting, A.B., & Zavarin, M. (*2020)* Transformation of Ferrihydrite to Goethite and the Fate of Plutonium. *ACS Earth Space Chem 4:11,1193-2006. https://doi.org/10.1021/acsearthspacechem.0c00195*
7. Zhao, P., Zavarin, M., Dai, Z., & Kersting, A.B. *(2020)* Stability of Plutonium Oxide Nanoparticles in the Presence of Montmorillonite and Implications to Colloid Facilitated Transport. *Appl. Geochem., 122: 104708.* https://doi.org/10.1016/j.apgeochem.2020.104725
8. Balboni, E., Smith K.F., Moreau L., Wimpenny J., Booth, C., Kersting A., M. Zavarin Plutonium co-precipitation with calcite. submitted to ACS Earth and Space Chemistry (2021)
9. Merino, N., Jackson, T.R., Campbell, J.H., Kersting, A.B., Sackett, J., Zavarin, M., Hamilton-Brehm, S.D., Moser, D.P. (submitted to PNAS (2021).
10. Dwivedi, D., Steefel, C., Arora, B., Banfield, J., Bargar, J., Boyanov, M.I., Brooks, S.C., Chen, X., Hubbard, S., Kaplan, D., Kemner, K.M., O'Loughlin, E.J., Pierce, E.M., Painter, S.L., Scheibe, T., Wainwright, H., Williams, K.H., and Zavarin, M. From Legacy Contamination to Watershed Systems Science: A Review of Scientific Insights and Technologies Developed through DOE-Supported Research in Water and Energy Security, (Submitted to Environmental Research Letters).

4.a.iii Publication Statistics

Of the 10 manuscripts completed during this review period, 7 were published (one invited) and 3 were submitted for review. Our research crosses many fields, from hydrology to basic chemistry, to microbiology (Table 4). To reach a wide audience and maintain LLNL's leadership role in environmental radiochemistry, our results have been published across a broad range of journals. In addition to our publications, we gave 8 virtual talks at universities and international meetings (6 invited). We also led a team of scientists from the various SFA's that submitted a white paper to the DOE BER Earth and Environmental Systems Science Division (EESSD) call for white papers to advance an integrative artificial intelligence framework for earth system predictability (AI4ESP) entitled "Process Discovery through Assimilation of Complex Biogeochemical Datasets" by M. Zavarin (LLNL), H. Wainwright (LBNL), P. Nico (LBNL), C. Steefel (LBNL), C. Varadharajan (LBNL), J.R. Bargar (SSRL), J. Damerow (LBNL), N.D. Ward (PNNL), V.L. Bailey (PNNL), and K.M. Kemner (ANL). This white paper outlines opportunities to apply machine learning to biogeochemical process models and data to advance watershed system science and reactive transport models. The application of machine learning in reactive transport modeling is a new theme in our SFA, as described below.

Table 4. Publication Statistics

Journal	Pubs	Impact Factor
PNAS	1[b]	9.4
Env. Sci & Tech	2	7.8
Env. Res. Letters	1[b]	6.2
Comm. Chem	1[a]	5.8
ACS Earth Space Chem	3[b]	3.6
Appl. Geochem	1	2.9
Data Sci. Journal	1	1.2

[a] Invited
[b] includes submitted manuscript

4.b Future Scientific Goals, Vision and Plans

The expanded mission of LLNL's Biogeochemistry at Interfaces SFA is to identify the dominant biogeochemical processes and the underlying mechanisms that control actinide and metal cycling across transient redox gradients. Our strategic goal is to use our new knowledge gained from this Science Plan to advance our understanding of the behavior of redox sensitive actinides and metals, 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 shifted to a field-oriented research program and a broader focus on metal cycling. We have taken that approach across all the focus areas and are focusing our research on environmentally relevant (e.g., decadal) timescales and associated processes. This shift in focus is allowing us 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 radiochemistry and environmental science research and education.

4.c New Scientific Results

New Scientific Results	Identified Gaps in Knowledge for Future Investigation
Discovered how bacterial surfaces can facilitate the precipitation of U-phosphate minerals by providing a local environment that is supersaturated with respect to U-phosphate minerals	Can this process impact metal cycling at environmentally relevant timescales?
Identified that reducing conditions lead to Pu mobilization in estuaries	How might this impact metal cycling in climate-impacted coastal systems?
Identified enhanced Fenton-type oxidation potential in the presence of organic matter	Does this process facilitate metal oxidation in surface waters?
Identified how subsurface planktonic microbial communities reflect regional-scale groundwater hydraulic connectivity	Can regional scale microbial community composition patterns be used to identify temporal and spatial groundwater flow patterns?

4.d Collaborative Research Activities

We had 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 and supervises the field campaigns at SRS. A second subcontract was with Dr. C. Booth at Lawrence Berkeley National Laboratory ($85K/yr). This subcontract supported a postdoc at 0.5 FTE. Due to our increased focus on field-oriented research, we do not plan to extend the LBNL subcontract into FY22. In addition to the funded collaborators, several groups are participating as unfunded collaborators. Dr. Gareth Law (U. of Helsinki and previously at Manchester University) is helping to wrap up our efforts at the Ravenglass estuary. D. Kaplan (SRNL) has deep insight into the history of Pond B and is providing support with coordinating field work at that site. N. Wall (Univ. of Florida) and her graduate student (Emily Maulden) are supporting our efforts at the Hanford site. C. Pierce (PNNL) is supported through PNNL's environmental management program (Vickie Freedman) and providing guidance for our efforts at the Hanford site.

4.e Data Management

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, Nancy Merino serves on the new Environmental System Science Data Infrastructure for a Virtual Ecosystem (ESS- DIVE, https://data.ess-dive.lbl.gov/) Archive Committee We were part of ESS-DIVE's pilot program to develop an inter-operable system for standardizing metadata and sample identifiers (Damerow, 2021), 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 campaigns and data analyses. We are also working with the ESS-DIVE committees to format our data in their chosen standardized format for the in-situ water column profiles and microbial community analyses. Currently, we have created two SRS Pond B databases to reflect the broad compartments of Pond B: the water column and sediments, and we are in the process of creating a portal for all BioGeoChemistry at Interfaces SFA related projects. The current metadata, protocols, and geochemical analyses have been uploaded to ESS-DIVE. The raw sequence files for microbial community analyses will be uploaded to the National Center for Biotechnology Information (NCBI) database and linked to our SRS Pond B ESS-DIVE page. In addition, these data will be made publicly available within two years on July 1, 2021, and the respective DOI number will be linked to our upcoming peer-reviewed publications.

5. STAFFING AND BUDGET SUMMARY

5.a Funding Allocation by Program Element

5.a.i Present Funding

In FY21 our SFA budget was $1.1M. LLNL staff effort and estimated total costs for June 2020-June 2021 are detailed Table 5. Note that total spending over this period amounted to $1.2M due to spend down of carryover funding.

Table 5. Cost breakdown for staff and Focus Areas.

Focus Area	Costs ($K)[d]	LLNL Researcher	Effort[c] (%)	Cost ($K)
1A	200	Annie Kersting	1	12
1B	100	Mavrik Zavarin	11	94
1C	150	Yongqin Jiao	3	15
1D	350	Enrica Balboni	15	52
1E	50	Nancy Merino[b]	79	204
2A	150	Keith Morrison	6	26
2B	100	Teresa Baumer[b]	67	164
2C	100	Naomi Wasserman[b]	57	146
		Paul Wooddy	6	12
Total	1.2M[a]	Administrator	13	29
		Other	9	32
		Total		**786**

[a] Includes costs of subcontracts to Clemson (110K) and Lawrence Berkeley National Laboratory (91K) as well as travel (1.3K) and procurements (196K).

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

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

[d] Relative allocation values.

5.a.ii Funding Changes

No changes in the overall funding of program elements were made this fiscal year. Limited access to laboratories during the COVID-19 pandemic limited certain activities. Nevertheless, two postdocs were hired. Laboratory access for our SFA was also restored in early FY21, with new COVID-19 safety protocols in place. Due to the reduction in both travel and laboratory access, we redirected some FY20 funding towards the purchase of instrumentation, as described in the FY20 annual report. Costs associate with those purchases are reflected in the significant procurement budget shown in Table 5.

5.b Funding for External Collaborators

See 4.d for details.

5.b.i Universities & Industry

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. Dr. Powell is essential to our efforts at the SRS Test Bed and will continue through FY22.

5.b.ii National Laboratories

One subcontract is with Dr. C. Booth at Lawrence Berkeley National Laboratory ($85K/yr). This subcontract supported a postdoc at 0.5 FTE. The subcontract provided our SFA the needed expertise in synchrotron-based actinide spectroscopy and was extended through March 2021. The programmatic needs to XAS expertise were reevaluated in FY21 and we have chosen not to extend this subcontract into FY22. We will reevaluate this decision during our FY22 SFA project renewal discussions.

5.c Personnel Actions

5.c.i. New Hires

Teresa Baumer joined the “BioGeoChemistry at Interfaces” SFA lastS eptember. Teresa is leading the Hanford column experiments and assist in Thrust 2 laboratory experiments. Teresa Baumer has a B.S. in Chemistry from Saginaw Valley State University and Ph.D. in Earth Sciences from the University of Notre Dame. Her dissertation research was supported by an NEUP-IUP fellowship and focused on understanding europium, neptunium, and Pu interactions with aluminum (hydr)oxide minerals.

Naomi Wasserman joined the “BioGeoChemistry at Interfaces” SFA last September. Naomi is leading our mass spectrometry efforts to understand what isotopic fractionation of actinides and other metals can tell us about the transient redox conditions that exist at our watershed test beds in South Carolina (Savannah River Site Pond B) and Nevada (Nevada Test Site E tunnel ponds) and the impacts on water quality. Naomi Wasserman received her Ph.D. from the Department of Geology at the University of Illinois at Urbana-Champaign, studying the isotope geochemistry of redox-sensitive elements with Professor Thomas Johnson.

5.c.ii. Anticipated Future Hires

As our SFA program is shifting toward a more long-term and field oriented research program, we are envisioning a need for support in the areas of numerical modeling and watershed system hydrology. These two needs will be advanced at our next all hands meetings and in anticipation of a programmatic review in FY22. As a first step, we recently posted a position for a reactive transport modeler with machine learning expertise to join our team. Elliot Chang (UC Berkeley/LBNL) accepted a PD position and will be starting in July 2021. He will be helping to develop machine learning algorithms for modeling metal reactive transport in earth systems in collaboration with Dr. Haruko Wainwright (UC Berkeley/LBNL). This new hire is aligned with the AI4ESP white paper led by LLNL on ML applications in biogeochemistry. If successful, this new direction in our SFA will be highlighted in our FY22 renewal plans. However, significant effort in this area may require an increase in LLNL’s SFA budget in FY23.

5.c.iii. Releases

No staff or postdoc releases occurred during this reporting period.

5.c.iv. Recruitment and Retention Activities

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 six national and international research groups. We are also coordinating our research with Dr. Clara Chan (U. of Delaware) who is a recent recipient of a EESSD funding supporting research at the SRS Pond B site. Our SFA supports 3 LLNL postdocs (Nancy Merino, Teresa Baumer, and Naomi Wasserman). Previous postdocs, Dr. Morrison, Dr. Balboni, and Dr. Deblonde were converted to staff scientists. In addition, our subcontracts supported a postdoc at Lawrence Berkeley National Laboratory (Kurt Smith) and one staff scientist at Clemson University (Fanny Coutelot).

To strengthen and expand our university collaborations, we have leveraged the Seaborg Institute's longstanding Student Internship Program as well as the Office of Science SCGSR program and the GEM program. Each year about twenty students spend the summer at LLNL carrying out research in the areas of nuclear forensics and environmental radiochemistry. In the summer of 2020, undergraduates Nick Parham (Colorado) and Jaddalah Zouabe (UC Berkeley) participated in the development of surface complexation databases and ML algorithms for reactive transport modeling. This year, Rahul Kaukuntla (MIT) is continuing this research. Ian Colliard (Oregon State University) joined the Seaborg Institute in January 2021 through the SCGSR fellowship program and will continue as an intern through the summer of 2021, mentored by Gauthier Deblonde.

5.d National Laboratory Investments

LLNL continues to support the Seaborg Institute and its various outreach, internship, and visiting scientist programs. The LLNL SFA took advantage of this support to develop collaborations with a number of national and international institutions and host graduate students interested in LLNL SFA research (see 5.c.iv).

LLNL invested ~$1.7M to renovate our Seaborg Institute Laboratory where we carry out experiments with higher levels of radioactivity. This renovation was a complete rebuild of the laboratory as well as upgrades to our controlled atmosphere gloveboxes.

In FY21, LLNL University Relations office supported this SFA through two programs. The first was in support of a new collaboration with H. Murakami Wainwright (UC Berkeley) and an undergraduate student (Jadallah Zaouabe) "Integrating Machine-Learning Toolsets with Environmental Radiochemistry at the Seaborg Institute". The project focused on developing novel machine learning approaches to geochemical modeling. A second effort was postponed due to COVID-19 but will resume later this summer (July) and this is in support of a mini-sabbatical for Frank Yang (University of Nevada, Reno) to develop research collaborations in organic matter-mineral-bacteria interfacial redox reactions. This research is directly related to both the BioGeoChemistry at Interfaces SFA and the Microbes Persist SFA.

Newly renovated Seaborg Institute radiochemical laboratory includes 4 hoods, two glove boxes, and 70 linear feet of wet chemistry bench space.

LLNL generously supported the purchase of a state of the art (~$400K) micro RAMAN microscope for use in organic matter characterization efforts. The instrument was internally funded via a LLNL multi-programmatic investment (SIA ISCP project 21-PLS-018) The instrument is a "hybrid Senterra II" confocal Raman imaging microscope (Bruker). This model is equipped with 3 different laser sources (532, 785, 1064 nm), an autocalibration module, a temperature-controlled heating and cooling stage, high resolution gratings, polarization kits, and a comprehensive Raman spectra library for maximum flexibility and fast sample processing. Chemical identification, degradation studies, 2D and 3D mapping on a wide variety of materials will be possible with this new instrument (minerals, organics, polymers, oxides…)

5.d.i. Staffing & Expertise Needs

As our SFA program is shifting toward a more long-term and field oriented research program, we are envisioning a need for support in the areas of numerical modeling and watershed system hydrology. These two needs will be advanced at our next all hands meetings and in anticipation of a programmatic review in the coming year (see 5.c.ii).

5.d.ii. Facility/Infrastructure Changes and/or Needs

LLNL has invested in the renovation of the Seaborg Institute laboratories (see above). This renovation was completed in June 2021 and will play a key role in supporting the infrastructure needs of this SFA.

5.e Capital Equipment Needs

Capital equipment needs are not presently anticipated for this SFA. However, we have identified a long-term need to build out our soil organic carbon characterization capabilities. While significant improvements in capital equipment were made with the support from this SFA and internal LLNL investments (Agilent 8890 GC System, Edinburgh Instruments FLS1000 steady state and lifetime TCSPC fluorimeter, hybrid Senterra II” confocal Raman imaging microscope), we anticipate that additional capital equipment may be needed. In particular LC-MS and FTICR instrumentation play an essential role in organic matter characterization and access to these technologies remains limited at LLNL. These instruments can play a critical role in organic matter characterization for a number of BER SFAs at LLNL.

6. REFERENCES

Abdelouas, A., Lutze, W., Gong, W., Nuttall, E.H., Strietelmeier, B.A. and Travis, B.J. (2000) Biological reduction of uranium in groundwater and subsurface soil. Sci Total Environ 250, 21-35.

Adam, P. (2002) Saltmarshes in a time of change. Environ Conserv 29, 39-61.

Alberts, J.J., Pinder, J.E., Bowling, J.W., Nelson, D.M. and Orlandini, K.A. (1986) 239,240Pu, 241Am and 232Th in lakes: The effects of seasonal anoxia. Journal of Environmental Radioactivity 4, 167-176.

Ames, L.L. (1974). Pacific Northwest Laboratories Report.

Balboni, E., Morrison, J.M., Wang, Z., Engelhard, M.H. and Burns, P.C. (2015) Incorporation of Np(V) and U(VI) in carbonate and sulfate minerals crystallized from aqueous solution. Geochimica et Cosmochimica Acta 151, 133-149.

Begg, J.D., Zavarin, M. and Kersting, A.B. (2014) Plutonium Desorption from Mineral Surfaces at Environmental Concentrations of Hydrogen Peroxide. Environmental Science & Technology 48, 6201-6210.

Begg, J.D., Zavarin, M. and Kersting, A.B. (2017) Desorption of plutonium from montmorillonite: An experimental and modeling study. Geochimica Et Cosmochimica Acta 197, 278-293.

Begg, J.D., Zavarin, M., Zhao, P., Tumey, S.J., Powell, B. and Kersting, A.B. (2013) Pu(V) and Pu(IV) sorption to montmorillonite. Environmental Science & Technology 47, 5146-5153.

Buck, E.C. (2014) Radiochim. Acta 102, 1059.

Burton, P.J. and Yarnold, L.P. (1988) Remobilisation of actinides from intertidal sediments of the ravenglass estuary.

Caborn, J.A., Howard, B.J., Blowers, P. and Wright, S.M. (2016) Spatial trends on an ungrazed West Cumbrian saltmarsh of surface contamination by selected radionuclides over a 25 year period. Journal of Environmental Radioactivity 151, 94-104.

Cantrell, K.J. (2009) Transuranic Contamination in Sediment and Groundwater at the U.S. DOE Hanford Site. Pacific Northwest National Laboratory, Richland, WA.

Cantrell, K.J. and Riley, R.G. (2008). Pacific Northwest National Laboratories Report.

Croal, L.R., Johnson, C.M., Beard, B.L. and Newman, D.K. (2004) Iron isotope fractionation by Fe(II)-oxidizing photoautotrophic bacteria 11Associate editor: D. E. Canfield. Geochimica et Cosmochimica Acta 68, 1227-1242.

Damerow, J.E., Varadharajan, C., Boye, K., Brodie, E.L., Burrus, M., Chadwick, K.D., Crystal-Ornelas, R., Elbashandy, H., Alves, R.J.E., Ely, K.S., Goldman, A.E., Haberman, T., Hendrix, V., Kakalia, Z., Kemner, K.M., Kersting, A.B., Merino, N., O'Brien, F., Perzan, Z., Robles, E., Sorensen, P., Stegen, J.C., Walls, R.L., Weisenhorn, P., Zavarin, M. and Agarwal, D., (2021) Sample Identifiers and Metadata to Support Data Management and Reuse in Multidisciplinary Ecosystem Sciences. Data Science Journal 20, 11

Fedarko, M.W., Martino, C., Morton, J.T., González, A., Rahman, G., Marotz, C.A., Minich, J.J., Allen, E.E. and Knight, R. (2020) Visualizing ʼomic feature rankings and log-ratios using Qurro. NAR Genomics and Bioinformatics 2.

Felmy, A.R., Cantrell, K.J. and Conradson, S.D. (2010) Plutonium contamination issues in Hanford soils and sediments: Discharges from the Z-Plant (PFP) complex. Physics and Chemistry of the Earth 35, 292-297.

Geckeis, H., Zavarin, M., Salbu, B., Lind, O.C. and Skipperud, L. (2019) Chapter 25: Environmental Chemistry of Plutonium, in: Clark, D.L., Geeson, D.A., R.J. Hanrahan, J. (Eds.), Plutonium Handbook, 2nd edition ed. American Nuclear Society.

Hamilton, E.I. and Clarke, K.R. (1984) THE RECENT SEDIMENTATION HISTORY OF THE ESK ESTUARY, CUMBRIA, UK - THE APPLICATION OF RADIOCHRONOLOGY. Sci. Total Environ. 35, 325-386.

Heberling, F., Brendebach, B. and Bosbach, D. (2008a) Neptunium(V) adsorption to calcite. Journal of contaminant hydrology 102, 246-252.

Heberling, F., Denecke, M.A. and Bosbach, D. (2008b) Neptunium(V) coprecipitation with calcite. Environmental science & technology 42, 471-476.

Heberling, F., Scheinost, A.C. and Bosbach, D. (2011) Formation of a ternary neptunyl(V) biscarbonato inner-sphere sorption complex inhibits calcite growth rate. Journal of contaminant hydrology 124, 50-56.

Heising, S. and Schink, B. (1998) Phototrophic oxidation of ferrous iron by a Rhodomicrobium vannielii strain. Microbiology (Reading) 144 (Pt 8), 2263-2269.

Huckins-Gang, H.E. and Townsend, M. (2014) Geology and History of the Water-Containment Ponds at U12n, U12t, and U12e Tunnels, Rainier Mesa, Nevada National Security Site. National Nuclear Security Administration, Nevada Site Office, Las Vegas, NV.

Icopini, G.A., Anbar, A.D., Ruebush, S.S., Tien, M. and Brantley, S.L. (2004) Iron isotope fractionation during microbial reduction of iron: The importance of adsorption. Geology 32, 205-208.

Kelly, S.D., Rasbury, E.T., Chattopadhyay, S., Kropf, A.J. and Kemner, K.M. (2006) Evidence of a stable uranyl site in ancient organic-rich calcite. Environ Sci Technol 40, 2262-2268.

Kershaw, P.J., Woodhead, D.S., Lovett, M.B. and Leonard, K.S. (1995) Plutonium from European reprocessing operations — Its behaviour in the marine environment. Applied Radiation and Isotopes 46, 1121-1134.

Leonardi, N., Defne, Z., Ganju, N.K. and Fagherazzi, S. (2016) Salt marsh erosion rates and boundary features in a shallow Bay. Journal of Geophysical Research-Earth Surface 121.

Lloyd, J.R. (2003) Microbial reduction of metals and radionuclides. FEMS Microbiology Reviews 27, 411-425.

Lovley, D.R. and Phillips, E.J.P. (1986) Organic-Matter Mineralization with Reduction of Ferric Iron in Anaerobic Sediments. Appl Environ Microb 51, 683-689.

Lu, N., Cotter, C.R., Kitten, H.D., Bentley, J. and Triay, I.R. (1998) Reversibility of sorption of plutonium-239 onto hematite and goethite colloids. Radiochimica Acta 83, 167-173.

Lucey, J.A., Gouzy, A., Boust, D., Vintro, L.L., Bowden, L., Finegan, P.P., Kershaw, P.J. and Mitchell, P.I. (2004) Geochemical fractionation of plutonium in anoxic Irish Sea sediments using an optimised sequential extraction protocol. Applied Radiation and Isotopes 60, 379-385.

Mackenzie, A.B. and Scott, R.D. (1993) Sellafield Waste Radionuclides in Irish Sea Intertidal and Salt-Marsh Sediments. Environ Geochem Hlth 15, 173-184.

Mackenzie, A.B., Scott, R.D., Allan, R.L., Benshaban, Y.A., Cook, G.T. and Pulford, I.D. (1994) SEDIMENT RADIONUCLIDE PROFILES - IMPLICATIONS FOR MECHANISMS OF SELLAFIELD WASTE DISPERSAL IN THE IRISH SEA. Journal of Environmental Radioactivity 23, 39-69.

Marshall, T.A., Morris, K., Law, G.T.W., Livens, F.R., Mosselmans, J.F.W., Bots, P. and Shaw, S. (2014) Incorporation of Uranium into Hematite during Crystallization from Ferrihydrite. Environmental Science & Technology 48, 3724-3731.

McCartney, M., Kershaw, P.J., Woodhead, D.S. and Denoon, D.C. (1994) Artificial radionuclides in the surface sediments of the Irish Sea, 1968–1988. Sci. Total Environ. 141, 103-138.

Meece, D.E. and Benninger, L.K. (1993) The coprecipitation of Pu and other radionuclides with CaCO3. Geochimica Et Cosmochimica Acta 57, 1447-1458.

Morris, K., Butterworth, J.C. and Livens, F.R. (2000) Evidence for the Remobilization of Sellafield Waste Radionuclides in an Intertidal Salt Marsh, West Cumbria, U.K. Estuarine, Coastal and Shelf Science 51, 613-625.

Morton, J.T., Marotz, C., Washburne, A., Silverman, J., Zaramela, L.S., Edlund, A., Zengler, K. and Knight, R. (2019) Establishing microbial composition measurement standards with reference frames. Nature Communications 10, 2719.

Pinder, J.E., Alberts, J.J., Bowling, J.W., Nelson, D.M. and Orlandini, K.A. (1992) The annual cycle of plutonium in the water column of a warm, monomictic reservoir. Journal of Environmental Radioactivity 17, 59-81.

Powell, B.A., Fjeld, R.A., Kaplan, D.I., Coates, J.T. and Serkiz, S.M. (2005) Pu(V)O_2^+ adsorption and reduction by synthetic hematite and goethite. Environmental Science & Technology 39, 2107-2114.

Price, S.M. and Ames, L.L. (1975). Atlantic Richfield Hanford Company Report.

Reeder, R.J., Elzinga, E.J., Tait, C.D., Rector, K.D., Donohoe, R.J. and Morris, D.E. (2004) Site-specific incorporation of uranyl carbonate species at the calcite surface. Geochimica et Cosmochimica Acta 68, 4799-4808.

Reeder, R.J., Nugent, M., Tait, C.D., Morris, D.E., Heald, S.M., Beck, K.M., Hess, W.P. and Lanzirotti, A. (2001) Coprecipitation of uranium(VI) with calcite: XAFS, micro-XAS, and luminescence characterization. Geochimica et Cosmochimica Acta 65, 3491-3503.

Reynaud, J.-Y. and Dalrymple, R.W. (2012) Shallow-Marine Tidal Deposits, in: Davis Jr, R.A., Dalrymple, R.W. (Eds.), Principles of Tidal Sedimentology. Springer Netherlands, Dordrecht, pp. 335-369.

Russell, C.E., Gillespie, L. and Gillespie, D. (1993) Characterization of the Effluent Draining from U12E, U12N, and U12T Tunnels, Area 12, Nevada Test Site. Desert Research Institute.

Sanchez, A.L., Murray, J.W. and Sibley, T.H. (1985a) THE ADSORPTION OF PLUTONIUM-IV AND PLUTONIUM-V ON GOETHITE. Geochimica Et Cosmochimica Acta 49, 2297-2307.

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

Sturchio, N.C., Antonio, M.R., Soderholm, L., Sutton, S.R. and Brannon, J.C. (1998) Tetravalent uranium in calcite. Science 281, 971-973.

Swanner, E.D., Bayer, T., Wu, W., Hao, L., Obst, M., Sundman, A., Byrne, J.M., Michel, F.M., Kleinhanns, I.C., Kappler, A. and Schoenberg, R. (2017) Iron Isotope Fractionation during Fe(II) Oxidation Mediated by the Oxygen-Producing Marine Cyanobacterium Synechococcus PCC 7002. Environmental Science & Technology 51, 4897-4906.

Temmerman, S., Govers, G., Wartel, S. and Meire, P. (2004) Modelling estuarine variations in tidal marsh sedimentation: response to changing sea level and suspended sediment concentrations. Marine Geology 212, 1-19.

Tinnacher, R.M., Zavarin, M., Powell, B.A. and Kersting, A.B. (2011) Mobilization of actinides by dissolved organic compounds at the Nevada Test Site. Geochim. et Cosmochim. Acta.

Tompson, A.F.B., Zavarin, M., McNab, W.W., Carle, S.F., Shumaker, D.E., Lu, C., Sun, Y., Pawloski, G.A., Hu, Q. and Roberts, S.K. (2011) Hydrologic Source Term Processes and Models for Underground Nuclear Tests at Rainier Mesa and Shoshone Mountain, Nevada National Security Site (Rev. 1.0), United States.

Whicker, F.W., Pinder, J.E., Bowling, J.W., Alberts, J.J. and Brisbin, I.L. (1990) Distribution of Long-Lived Radionuclides in an Abandoned Reactor Cooling Reservoir. Ecological Monographs 60, 471-496.

Xu, J., Veeramani, H., Qafoku, N.P., Singh, G., Riquelme, M.V., Pruden, A., Kukkadapu, R.K., Gartman, B.N. and Hochella, M.F. (2017) Efficacy of acetate-amended biostimulation for uranium sequestration: Combined analysis of sediment/groundwater geochemistry and bacterial community structure. Applied Geochemistry 78, 172-185.

Zhao, P.H., Begg, J.D., Zavarin, M., Tumey, S.J., Williams, R., Dai, Z.R.R., Kips, R. and Kersting, A.B. (2016) Plutonium(IV) and (V) Sorption to Goethite at Sub-Femtomolar to Micromolar Concentrations: Redox Transformations and Surface Precipitation. Environmental Science & Technology 50, 6948-6956.