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LLNL SFA OBER FY23 Program Management and
Performance Report:

BioGeoChemistry at Interfaces

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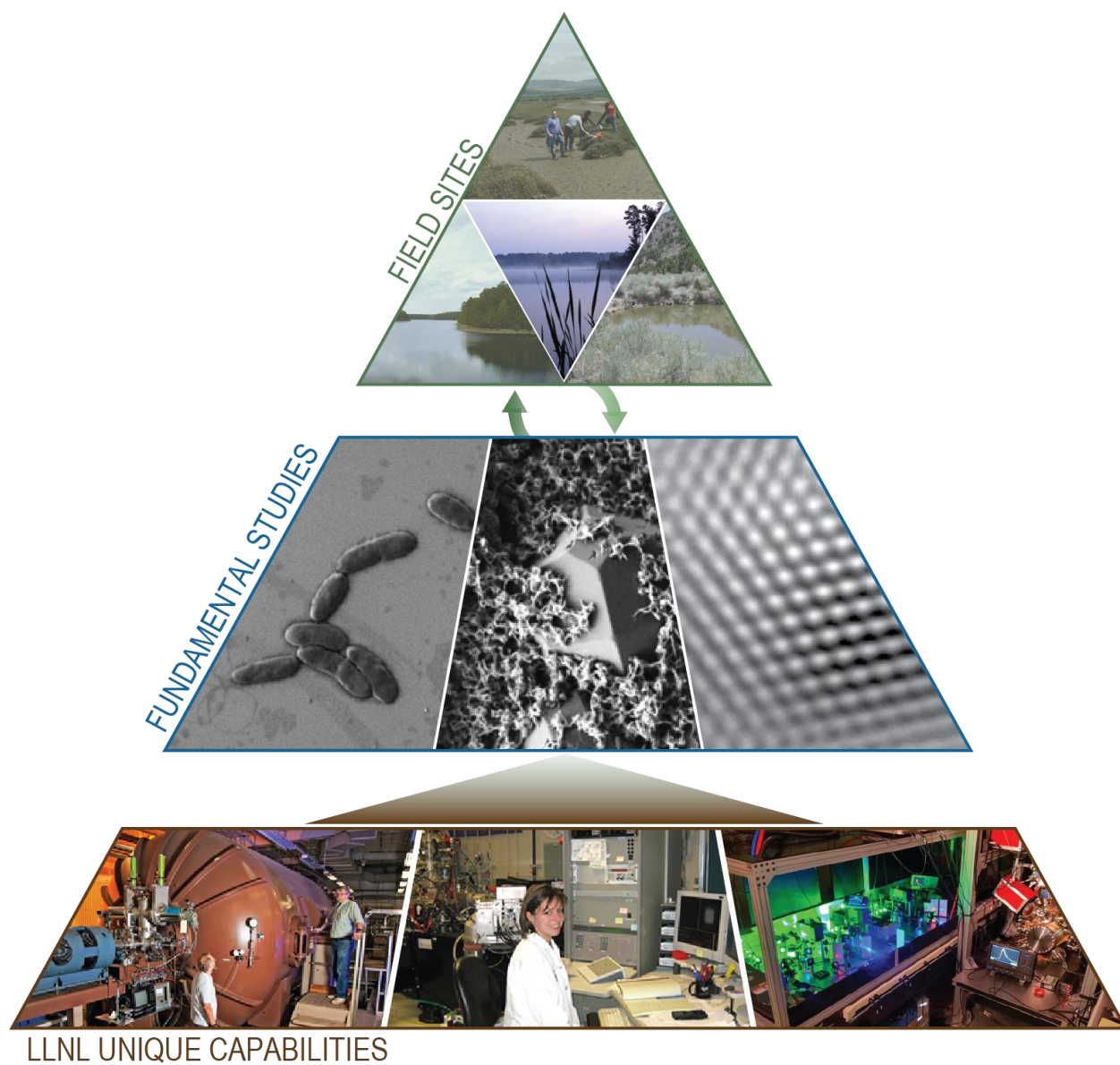


Figure 1. Integration of three core elements in the BioGeoChemistry at Interfaces Scientific Focus Area.

1. PROGRAM OVERVIEW

The focus of the BioGeoChemistry at Interfaces SFA has been 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 has included: (1) Field Studies that capture actinide behavior on the timescale of decades (Research Thrust 1), and (2) Fundamental Laboratory Studies that isolate specific biogeochemical processes observed in the field (Research Thrust 2). 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 a resource for environmental radiochemistry research internationally (Figure 1). In FY23, our SFA research focused on transient redox gradients across stratified waters, sediment-water interfaces, and mineral-water interfaces to address processes controlling cycling of redox-sensitive metals. Nevertheless, Research Thrusts 1 and 2 are guided by the following broad central hypotheses that were developed during our last program review held at the end of FY18:

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 and other radionuclides (e.g. Cs) and provide DOE with the scientific basis for remediation and long-term stewardship of DOE's legacy sites. More broadly, we are improving our understanding of transport phenomena in environmental systems sciences with a particular emphasis on environmentally relevant (long-term) timescales. While we retained some of our historical focus on actinide biogeochemistry this past fiscal year, biogeochemical processes occurring at unique Test Bed locations associated with this SFA provide fundamental information on abiotic and biotic redox processes that control the cycling of redox sensitive metals under dynamic and transient conditions. Furthermore, in collaboration with SFA teams at Argonne National Laboratory, our SFA has begun to transition away from the current research focus and develop a new research program in terrestrial wetland systems. ***The Terrestrial Wetland Function and Resilience SFA program plan will be delivered to the Environmental System Science (ESS) program within BER at the end of FY23.***

2. SCIENTIFIC OBJECTIVES

The goal of LLNL's present SFA has been to identify and quantify the biogeochemical processes that control the fate and transport of actinides in the environment. In FY23, our research supported the goals of the ESS program within BER to advance a robust, predictive understanding of how watersheds function as integrated hydro-biogeochemical systems, as well as how these systems respond to disturbances such as changes in water recharge, availability, and quantity; contaminant release and transport; nutrient loading; land use; and vegetative cover. We 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, and
- 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 some focus on actinides while strengthening its research in metals cycling at interfaces and planning for a transition to a new Terrestrial Wetland Function and Resilience SFA program in FY24.***

3. PROGRAM STRUCTURE

Dr. Felice Lightstone is the Laboratory Research Manager of LLNL's BER programs. She is group leader in the Biosciences and BioTechnology Division (BBTD) in the Physical and Life Sciences (PLS) directorate 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 biogeochemical system science, 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 several 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. Dr. Annie Kersting retired in April 2023 and returned to LLNL as a visiting scientist. As the SFA transitions to the Terrestrial Wetland Function and Resilience SFA, Dr. Kersting will transition away from participating in this program (see 5.c.iii).

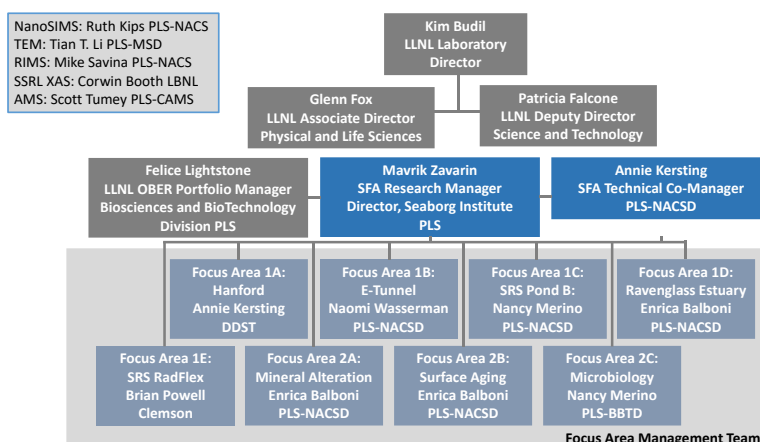


Figure 2. BioGeoChemistry at Interfaces SFA management organization.

3.A KEY PERSONNEL

Mavrik Zavarin—Director of the Glenn T. Seaborg Institute - Dr. Zavarin is 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. He is the Program Manager of this SFA and is responsible for overall planning and execution of the research program. Along with Dr. Kersting, 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.

Annie Kersting—Senior Scientist - Dr. Kersting is a geochemist with expertise in isotope geochemistry, actinide chemistry, colloid-facilitated transport, and field investigations of contaminant transport. She is the technical co-manager of this SFA and helps drive the research agenda with Dr. Zavarin. Together with Dr. Zavarin, she co-mentors the SFA postdocs. She leads Focus Area 1A: Hanford Z-9 trench.

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.

Enrica Balboni—LLNL staff scientist - Dr. Balboni is 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) and oversees all laboratory operations conducted as part of this SFA.

Nancy Merino—LLNL postdoctoral fellow converted to staff (June 2022) - Dr. Merino is a geobiologist with expertise in environmental microbiology, bioremediation, microbe-metal interactions, and bioinformatics. She 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.

Naomi Wasserman – LLNL postdoctoral fellow (started August 2020) - Dr. Wasserman is an isotope geochemist with a focus on redox geochemistry. She is studying Pu and Fe biogeochemistry at SRS (Focus Area 1C), and leads Focus Area 1D: NNSS E-Tunnel ponds.

Teresa Baumer – LLNL research scientist (postdoctoral fellow converted to staff) - Dr. Baumer is an analytical chemist with a focus on trace metals. She is studying Pu transport behavior at the Hanford site and examining the role of organic chelating solvents on its migration behavior (Focus Area 1A).

Elliot Chang – LLNL postdoctoral fellow (departed in March to lead research in carbon sequestration as part of Eion startup: <https://agfunder.com/portfolio/eion/>) - Dr. Chang is a geochemical modeler currently focusing on the intersection of machine learning (ML) and traditional surface complexation modeling. He is developing hybrid ML approaches to quantify metal-mineral sorption processes and is actively working towards automated, community-based data analytics.

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

Sol-Chan Han – LLNL postdoctoral fellow (started in November 2021) - Dr. Han is a nuclear engineer with expertise in reactive transport modeling. He has been working with Dr. Elliot Chang on the application of community sorption data and novel modeling workflows to develop self-consistent geochemical models of reactions at mineral-water interfaces.

4. PERFORMANCE MILESTONES AND METRICS

Table 1 shows the planned schedule for each task as identified in the FY22 progress report. Some scope has been extended into FY24 as part of our planned transition to a new SFA. The Hanford effort (Task 1A) is on track to be completed in FY23 with a manuscript published in FY24. The Ravenglass effort (Task 1B) was completed in FY22. The E-Tunnel effort at NNSS was delayed by COVID-19 travel restrictions but is now well underway and planned for completion in FY24. The field sampling campaign at SRS Pond B and associated research tasks will wind down in FY24. We anticipate that all tasks associated with this SFA will be complete in mid-FY24 as the new Terrestrial Wetland Function and Resilience SFA (SFA3) is initiated.

Table 1. Timeline for each task identified in this Science Plan.

	Focus Area and Task	FY19	FY20	FY21	FY22	FY23	FY24
THRUST 1: FIELD STUDIES – BIOGEOCHEMICAL PROCESSES AFFECTING ACTINIDE TRANSPORT IN THE ENVIRONMENT							
	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						*
	Task 1B-1: Characterization of Ravenglass estuary actinide profiles	*					
	Task 1B-2: The role of redox cycling on actinide mobilization in sediments				*		
	Task 1C-1: Characterization of E-Tunnel pond actinide profiles					*	
	Task 1C-2: Advective transport through pond sediments						*
THRUST 2: FUNDAMENTAL PROCESSES – ACTINIDE STABILIZATION AT ENVIRONMENTALLY RELEVANT TIMESCALES							
	Task 2A-1: Pu incorporation in iron oxides and calcium carbonate			*			
	Task 2A-2: Formation of actinide-Al solution complexes						
	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		*				*
	Task 2C-1: Characterization of microbial exudates and their interaction with Pu					*	*
	Task 2C-2: Pu (im)mobilization from mineral surfaces by microbial exudates						
	Task 2C-3: Pu stabilization by microbial macromolecules on mineral surfaces					*	
	Task 2C-4: Pu incorporation into iron oxides of microbial origin					*	

extension; delay; planned; * milestone

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 focuses on investigating the role of kinetically slow and/or irreversible biogeochemical 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 long-term actinide migration using field site contaminant migration histories.

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 $^{239/240}\text{Pu}$ 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.; Oxid.
Sellafield/Ravenglass Estuary, Irish Sea UK	1952-Present 3,240 Ci ^{238}Pu ; 16,500 Ci $^{239/240}\text{Pu}$; 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 precipitation 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; Oxid.
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; Seasonal anoxia.
RadFlex SRS SC	2012-Present; 0.013 Ci $^{239/240}\text{Pu}$ 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	Oxid, unsaturated zone, highly-weathered sandy loam/sandy clay loam soil, pH ~5

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

Lead: A. Kersting, contributors: T. Baumer, C. Pearce

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 (~ 4×10^6 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 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 have been completed (Baumer et al., 2022). Task 1A-3, Pu reprocessing waste reactive transport through sediments, builds on the data obtained in Task 1A-1 and 1A-2. Originally delayed due to staffing issues, this Focus Area is back on track and will be completed in FY23.

Task 1A-1 and 1A-2: Pu complexation with reprocessing waste and reactions between sediments and Pu reprocessing waste

The majority of the work for Task 1A-1 was reported in FY20 and FY21. This task focused on identifying which components of the waste stream and sediments 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 and ternary batch experiments between an aqueous phase and organic phase and the mineral albite as a function of pH (2 to 8). Our results showed that Pu at equilibrium with low pH, high nitrate waste and in the presence of a TBP/organic phase can migrate as a Pu-TBP-nitrate complex in the organic phase as long as the low pH and high nitrate concentrations are maintained. Reducing the nitrate concentrations or increasing the pH will lead to Pu partitioning into the aqueous phase with subsequent sorption to native Hanford sediments. The results of this work suggest that Pu migration in the subsurface is likely driven by weak sorption of aqueous Pu under low pH conditions as well as the formation of Pu-TBP-nitrate complexes in the organic phase. Long-term Pu migration will be limited by the transient nature of low pH conditions and dispersion of the nitrate plume. The results were published in Applied Geochemistry (Baumer et al., 2022).

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 waste solutions. Uncontaminated sediment from the Hanford Site was obtained from the Pacific Northwest National Lab soil library and loaded into glass sediment columns.

Saturated column experiments were used to investigate the two main disposal scenarios: 1) Pu mobility in low pH, high ionic strength aqueous fluids, and 2) Pu mobility in mixed low pH, high ionic strength aqueous fluids plus organic TBP-containing solvents. Tritium (^3H) was used as a tracer for all experiments. Three aqueous columns were designed to investigate Pu mobility in 5 M NaNO_3 at pH 2.5, pH 1.5, and pH 1.0. The low pH Pu/ ^3H -containing 5 M NaNO_3 solutions were introduced into the column immediately after conditioning with the synthetic pore fluid. Figure 3A shows the Pu and ^3H concentrations measured in the effluent normalized to initial concentration (C/C_0) with respect to pore volume in the pH 1 aqueous system. In this system, the Pu eluted from the column when the sediment was reduced to pH < 4 and significant Pu mobility was observed at pH < 2. A total of 14% Pu breakthrough was observed in this case.

To understand Pu mobility in a low pH, high ionic strength aqueous fluids with the addition of an organic, TBP-containing solvent, three column experiments were prepared in which Pu was introduced into the column in a 15% TBP/dodecane solution. Two of these mixed organic/aqueous columns were prepared by first

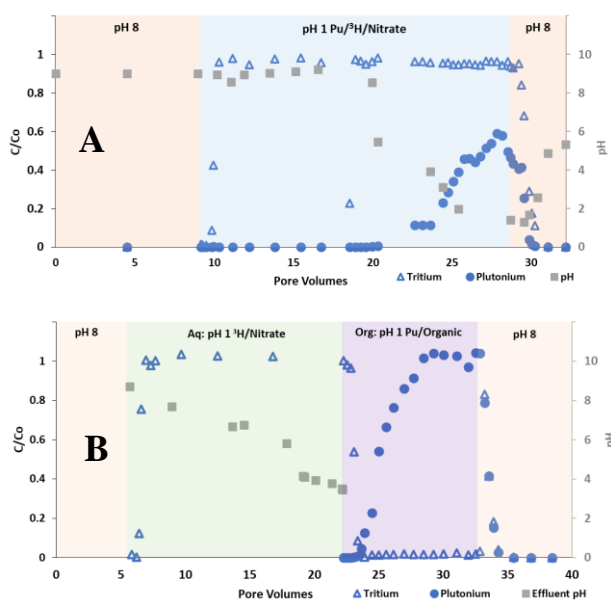


Figure 3 (A) Effluent pH and Pu concentration in sediment column reacted with Pu-bearing - 5 M NaNO_3 - pH 1 simulated waste and (B) Pu-bearing - 15% TBP/dodecane at pH 3.5.

“acid-treating” the sediments with a pH 1, 5 M NaNO₃ solution until the effluent pH decreased to 3.5 or 1 before the Pu-containing organic solutions were introduced into the column. This resulted in removing the buffering capacity of the sediments to replicate the scenario in the trench in which acidic waste flowed through the sediments followed by Pu-containing organic solvents. Figure 3B shows the normalized Pu and ³H concentrations with respect to pore volume for the mixed organic/aqueous column experiment at pH 3.5. Pu breakthrough was observed within one pore volume of being introduced into the column (at approximately 23 pore volumes). The Pu traveled virtually unhindered through the acid treated sediments with nearly 86% total Pu elution. These experiments show that Pu can be mobilized in the columns in both the aqueous and organic solutions once the pH of the sediments is reduced to pH < 4. However, significantly more Pu can be eluted from the columns in the presence of organic solvents. These results provide direct evidence for the likely mechanisms that drove Pu migration to significant depths (~37m) at the Z-9 trench and provides the scientific basis to predict the risks of groundwater contamination at this site. A manuscript is in preparation and is expected to be published in the Fall of 2023.

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 northwest coast of England was originally established in 1947 to support the UK nuclear weapons program (Figure 4). 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 4). The radionuclides from the mud-patch have been redispersed via particulate transport in fine-grained estuarine and intertidal sediments in the North-East Irish sea (Hamilton and Clarke, 1984; Kershaw et al., 1995; Mackenzie et al., 1994) including the Ravenglass estuary (Burton and Yarnold, 1988; Caborn et al., 2016; Lucey et al., 2004; Mackenzie and Scott, 1993; Mackenzie et al., 1994).

The Ravenglass saltmarsh is located 10 km south of the Sellafield site and is a low energy, intertidal region that accumulates Sellafield-derived contamination (Hamilton and Clarke, 1984). 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. Results of this work were published in FY22 and are briefly summarized below (Balboni et al., 2022).

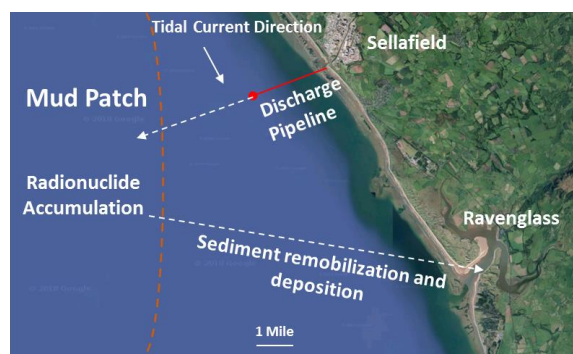


Figure 4. Location of the Sellafield site, mud patch, and Ravenglass Estuary (McCartney et al., 1994; Reynaud and Dalrymple, 2012).

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

The sediment core collected from the Ravensglass saltmarsh in 2017 was 30 cm in length and shipped to LLNL where it was stored under controlled conditions. It was subsequently divided in six, 5 cm layers, and used to determine the vertical distribution of radionuclides (Pu, Am, Cs). Plutonium reached a maximum concentration at 10-15 cm (Figure 5) and then dropped sharply approaching detection limits at 25 cm. Overall, the radionuclides' distribution and Pu isotope ratios measured in the sediment profiles suggest that multiple processes play a role in their distribution patterns. These processes may include variable sedimentation rates, lateral variation in radionuclide concentration, lateral transport of contaminated sediments and vertical mixing within the sediment profile.

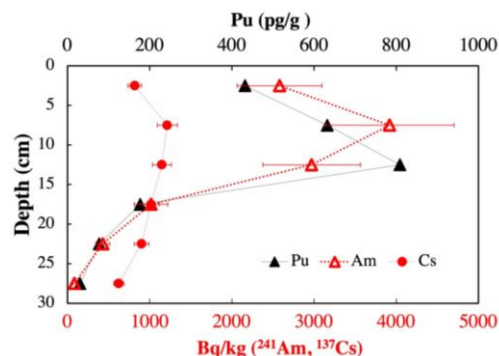


Figure 5. distribution of $^{239,240}\text{Pu}$, Am & Cs concentration in Ravensglass sediments with depth.

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

The goal of this task was to examine the factors affecting the mobility of Pu in redox stratified sediments by conducting desorption experiments of contaminated Ravensglass sediments under both oxic and anoxic conditions. Desorption experiments were conducted over a nine-month period. Desorbed Pu (measured by multi-collector ICP-MS) and redox indicators (Eh, pH and extractable Fe(II)) were monitored. All Pu desorption data are reported in Figure 6. Under anoxic conditions and in the top sediment layer (0-5 cm) the concentration of desorbed Pu was highest at 1 month and decreased thereafter. However, not much difference in Pu desorption behavior was observed in the deeper sediments.

Plutonium leaching was about three times greater in solutions leached under anoxic conditions compared to oxic conditions. Under oxic conditions, less Pu was desorbed from the sediments at every depth compared to the anoxic system. Interestingly, the highest amount of Pu leached from the sediments in both anoxic and oxic experiments was observed in the shallowest sediments (0-10 cm) while the highest sediment Pu concentrations were found at a greater depth of 10-15 cm. Thus, it appears that the mobilization of Pu is not correlated to total Pu content in the sediments. As the top sections represent younger Sellafield deposition, Pu may be associated with younger, more labile organic material. We hypothesize that Pu leaching from sediments will tend to decrease with sediment age and depth, as Pu associations and organic matter composition becomes more stable. Characterization of the microbial community showed variation between the different Ravensglass microcosms and is largely explained by variations in anoxic/oxic conditions (Balboni et al., 2022). This suggests that anaerobic biotic processes contributed to the consistently higher Pu mobilization observed in anoxic versus oxic sediments. These findings provide constraints on the stability of redox sensitive Pu in biogeochemically dynamic/transient environments on a timescale of months and suggests that anoxic conditions can enhance Pu mobility in estuarine systems.

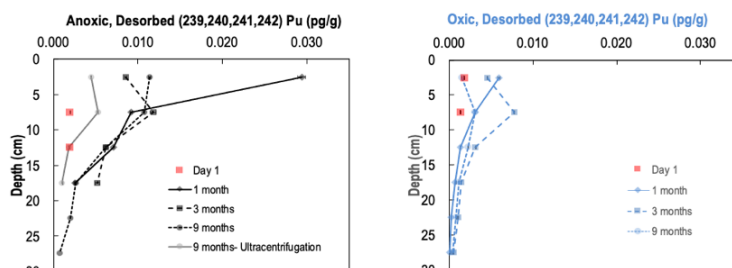


Figure 6 Left: Pu desorption from anoxic (left) and oxic (right) sediments up until 9 months.

Focus Area 1C: NNSS E-Tunnel pond actinide migration*Lead: N. Wasserman; contributors: N. Merino, K. Morrison*

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 (Figure 7). While radionuclide concentrations in the discharge remain below permissible limits (with the exception of tritium), 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). The ponds not receiving E-Tunnel discharge are primarily dry with the exception of inputs from precipitation during spring and summer monsoons. The shallow sediments 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).



Figure 7. Map of sample locations where water and sediments samples were collected during April 2022. Dark blue indicates sediment core (13) and light blue indicates water sample (5) locations.

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 and will be completed FY23. The second task, which was started in FY23, is to examine the role of advective transport in mobilizing contaminants across the pond-sediment interface and into the underlying regional carbonate aquifer.

A third study, initially started in 2008, completed in FY22 investigated whether or not the planktonic microbiome in groundwater can reflect groundwater flow paths identified by regional groundwater models and also reveal perturbations to a groundwater basin not captured by hydrogeochemical data alone. We examined the groundwater microbial communities of southern Nevada, specifically the Death Valley Regional Flow System (DVRFS). Using ordinations, network and null model analyses, we determined that the groundwater microbiome can reflect groundwater flow paths identified by regional groundwater models. Our work demonstrates the utility of including microbial community datasets as a data source for comprehensively characterizing groundwater systems. This work was published on June 21, 2022 (Merino et al., 2022) and summarized in detail in our FY22 annual report.

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

Previously, we reported the collection of thirteen, 1 ft cores in four ponds and several filtered and unfiltered water samples in April 2022 (Figure 7). In Pond 2 (oldest contamination), we cored to the dolomite bedrock underlying the pond sediments and collected fragments of the formation. Ponds 6b and 6c (newest contamination), which presently receive water from E-Tunnel, contain abundant plant life. Cores collected in these ponds have thick organic -rich horizons as opposed to Ponds 5 and 2 which do not. Organic matter can impact radionuclide mobility as Pu has strong affinity for organic matter, while Cs does not (Mihalik et al., 2014). Another important control on both Cs and Pu transport may be sorption to certain clay minerals. In this task, we examined ^{137}Cs and Pu distribution vertically in these sediments along with total organic carbon, mineralogy, and grain size distribution. A PhD student from the University of Central Florida mentored by Naomi Wasserman assisted with these analyses in the summer of FY22. Our XRD results show that the alluvial sediment is dominantly a weathered product of the surrounding volcanic tuff with some contribution from the dolomite bedrock (Figure 8). Importantly, zeolites are a major component of the core sediments, which may incorporate Pu in their structure. While the expected inventory of ^{137}Cs should be highest in Pond 2, cores from Pond 5 contains the highest ^{137}Cs concentrations followed by those from Pond 2 then 6b. Furthermore, ^{137}Cs concentrations are highest at the top of the cores except for Pond 2 indicating that ^{137}Cs is not completely immobilized in the sediments over decades (Figure 9). Plutonium concentrations are highest in the first 5 cm in all cores and appear to be immobile (not shown). We expect to finish our core characterization in late FY23. These efforts will include autoradiography to identify the presence of any hot particles in the sediments, and GC/MS to examine the fraction of anthropogenic hydrocarbons in the sediments from historic oil spills at this site. Our results will inform future experiments and models to examine advective transport in Task 1C-2.

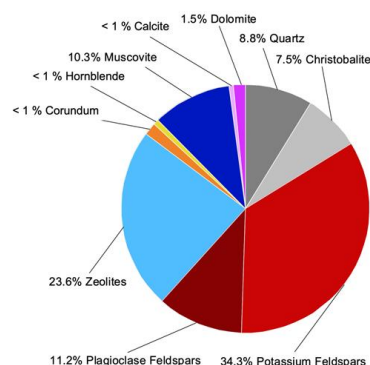


Figure 8. Average mineral composition of E-Tunnel sediment cores by quantitative XRD.

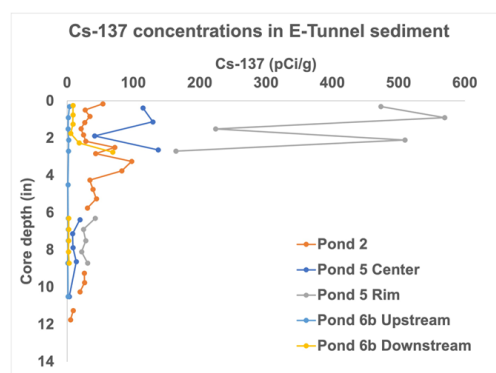


Figure 9. Cesium-137 concentrations in five cores from Pond 2, Pond 5, and Pond 6b.

Task 1C-2: Advective transport through pond sediments

Advective flow from rainwater infiltration has the potential to remobilize radionuclides in the E-Tunnel sediments and could lead to a long-term source of contaminants to the underlying dolomite-hosted aquifer. At our site, seasonal monsoons followed by long periods of minimal precipitation could induce subsurface redox cycling, which may mobilize Cs and Pu through colloid generation (Kersting et al., 1999; Thompson et al., 2006) and Pu association with dissolved organic matter (Santschi et al., 2002). However, previous work from our group has shown that certain radionuclides, like Pu, can form recalcitrant phases in organic-rich iron phases (Balboni et al., 2022). In addition, the Pu deposited in the sediments from the E-Tunnel groundwater may be effectively immobilized in clays or zeolites that are present in the pond sediments (Joseph et al., 2019). We will conduct a series of flow-through column experiments in early FY24 to (1) quantify the fractions of Pu and Cs that are released during wet-dry cycles, (2) examine what mineralogical and geochemical associations influence radionuclide remobilization, and (3) investigate how the characteristics of radionuclides native to E-Tunnel influence contaminant transport. Sediment collected from Ponds 2 (contaminated 1950's-1970s, little vegetation) and 6B (actively receiving E-Tunnel discharge, high vegetation) will be dry packed into separate glass columns. Synthetic rainwater (low ionic, slightly acidic) spiked with ^3H will be pumped through the columns. Effluent from the columns will be measured for radionuclide concentrations, presence of colloids, and dissolved organic carbon. After radionuclide breakthrough, the columns will be left open to air and allowed to dry completely followed by a second rainwater inundation. Each column will be deconstructed after the flow-through experiment has concluded.

for radionuclide profile measurements and associations with certain mineral phases, which will be compared to our results from Task 1C-1. To address the third objective, ^{238}Pu and ^{137}Cs will be added to sediment from Pond 6b. Effluent collected from a similar flow-through experiment using synthetic rainwater will test whether the radionuclides present as free ions are remobilized differently than the native Pu and Cs.

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

Lead: B. Powell, contributors: N. Merino F. Coutelot, N. Wasserman, J. Wheeler, and D. Kaplan

Pond B at Savannah River Site (SRS) is an ideal location for tracing the biogeochemical cycling of C, trace elements, and Pu that was released into the Pond system approximately 60 years ago for a period of ~7 years. Pond B received SRS R reactor cooling water between 1957–1964 containing $^{238,239,240}\text{Pu}$, ^{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.

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 (water and sediments). 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 a manuscript describing the temporal behavior of Pu and Cs in the sediments has recently been published (Coutelot et al., 2023).

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

Our quarterly sampling efforts have continued in FY23 with measurements taken of biogeochemical parameters (e.g., pH, dissolved oxygen, temperature, and 8 others) and a new emphasis on quantitatively filtering samples to determine suspended particle concentrations and associated Pu and trace element concentrations. In pond B, thermal stratification gradually develops in early April and lasts until late November, with a maximum difference in water temperature between the surface and bottom layers reaching more than 15 °C; environmental conditions such as warm air temperature and weak winds contribute to stratification onset. Strong thermal stratification forms a distinct thermocline in May, progressing downwards until November. The strong thermocline still present in the November 2022 sampling is shown by the geochemical parameters, pH, ORP, and temperature in Figure 10.

As described in FY22, we measured the Pu concentrations (as $^{240,239}\text{Pu}$) and Pu isotope ratios of unfiltered water samples during peak stratification (June 2019), and during an unstratified period (March 2020). Pu concentrations increased slightly with depth during stratification similar to previous observations of Alberts *et al.*, (1987). Interestingly, water column Pu profiles were similar in concentration or higher when Pond B was not stratified. Additional thermodynamic modeling and Principal Component Analysis of Pond B geochemical parameters indicate that Pu release is primarily controlled by the release from sediments. Instead, our analysis of the Pu water column inventory by season suggests that most of the Pond B Pu exists in the shallow water column (0-6 m) and peaks in early spring before stratification. Plutonium in the deeper water (6-12 m) peaks in early summer coinciding with onset of complete pond stratification as a result of reductive dissolution of pond sediments. Comparisons with the sediment data (Coutelot et al., 2023) and previous water column measurements (Pinder et al., 1992) indicate that the majority of Pu remains within the sediments and may be increasingly

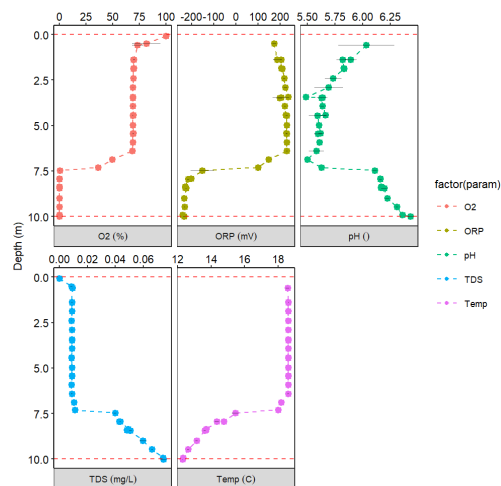


Figure 10. Oxygen, ORP, pH, Total dissolved solid (TDS), and water temperature as a function of depth at the deepest location of the pond. November 2022 field sampling.

recalcitrant over time. A manuscript detailing these results was just accepted in Nature Scientific Reports (Wasserman et al., Accepted).

In FY23, the variation in the particulate fraction of the water column was investigated as a function the season. A water filtration protocol was designed to collect filtrate samples in the field to preserve the integrity of the chemistry of samples. Concurrently, water chemistry measurements were conducted using sonde probes, encompassing pH, ORP, and dissolved oxygen levels, and the particulate fractions of the water column (1.2 μ m for debris, 0.45 μ m for colloidal fraction and through a 0.22 μ m for truly dissolved fraction). Results show the presence of a thermocline in the lake associated with an anoxic zone at the bottom of the lake which had a major influence on dissolved oxygen concentrations and iron concentrations (Figure 11). Notably, the anoxic zone displayed a discernible size dependence in iron and arsenic concentration, indicating the introduction of ferrous iron particulate into the hypolimnion during the summer (Figure 12). These particles are expected to oxidize to form ferric hydroxide precipitates in winter when the pond becomes well-mixed. The observed vertical size distribution pattern of iron and arsenic is believed to be attributed to iron-bearing aggregates settling below the thermocline and facilitating the sequestration of trace elements. Preliminary spectroscopic results indicate the presence of iron and organic matter in the aggregates. These preliminary results highlight the complexity of the water column dynamics and the potential role of iron-bearing aggregates and organic matter in shaping the distribution of particulate fractions in pond B.

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

Concentrations

In FY22 and FY23, there was a major effort to collect sediments samples in the R-canal and in Pond B to assess the correlations between ^{239}Pu concentrations with other geochemical factors such as sediment type, organic matter content, and major/minor element composition. We have completed that sampling program with 50 samples collected throughout the system and noted that the concentrations of ^{239}Pu are much greater in Pond B than in the R-canal suggesting a high degree of sediment transport occurring and/or poor attenuation of ^{239}Pu in the canal sediments (Table 3, Figure 13). The former is consistent with the high volumes of water released to Pond B during reactor operation.

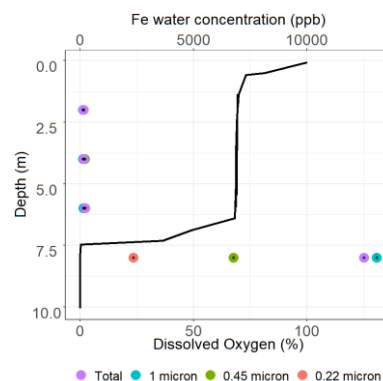


Figure 11. Dots represent iron concentration in filtrate from water column samples, and the black line is the dissolved oxygen levels in the water column sampled at the deepest depth location in pond B.

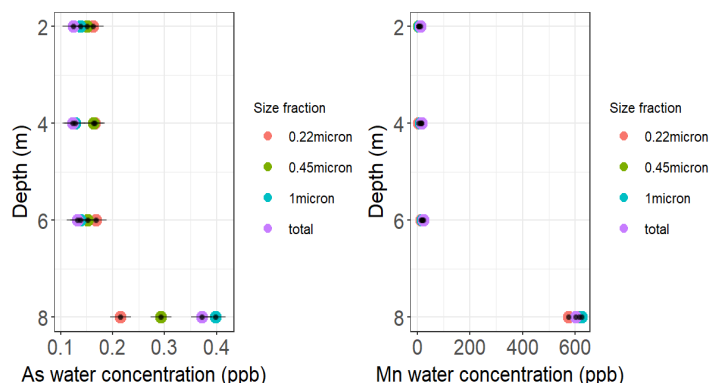


Figure 12. Arsenic and manganese concentration in filtrate (1 μ m, 0.45 μ m and 0.22 μ m size fraction) over the water column depth at the deepest depth in pond B.

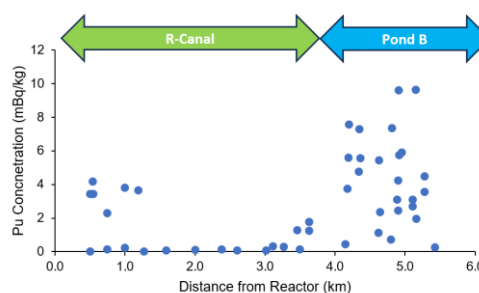


Figure 13. Concentrations of ^{239}Pu as a function of distance from the R-reactor

Correlations between ^{239}Pu and other geochemical parameters are currently being evaluated using principal component analysis. In addition, GIS mapping is being used to compare the total inventory of ^{239}Pu and ^{137}Cs in Pond B with historical estimates. Preliminary calculations with ^{137}Cs maps show, 1) a potential correlation between ^{137}Cs distributions with natural organic matter concentrations, and 2) a means of extrapolating a total ^{137}Cs activity in the Pond (Figure 14). The total ^{137}Cs calculated from this effort is comparable to historical estimates (Mohler et al., 1997; Whicker et al., 1990) indicating that over the past 40 years only a minimal amount of ^{137}Cs has migrated out of Pond B. A similar GIS based approach is underway for analysis of ^{239}Pu and trace metals.

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

Previously, we determined that the Pond B water column microbial community varies with depth rather than location during stratification and can be categorized by the three distinct stratification layers. The stratified microbiome evolves throughout the stratification period from June to October. During spring turnover, the microbiome is similar throughout Pond B, reflecting the uniform geochemistry of the well-mixed pond water (e.g., uniform oxygen concentrations, temperature, metals).

We further examined the differences between the hypolimnion microbial communities between June and October by using a software called Songbird (Morton et al., 2019). This software is a multinomial regression tool that ranks operational taxonomic units (OTU) differential abundances in association with other factors. Notably, the whole Pond B water column microbiome dataset is associated with iron concentrations and could be categorized into four groups: ‘low Fe’ (0–0.009 mM), ‘low-mid Fe’ (0.009–0.04 mM), ‘mid Fe’ (0.04–0.18 mM), and ‘high Fe’ (>0.18 mM). We then evaluated the OTU ranks associated with ‘mid Fe (0.04–0.18 mM)’ and ‘high Fe (>0.18 mM)’ to assess the hypolimnetic stratified communities (Figure 15). Overall, more putative aerobes or microaerophiles were associated with ‘mid Fe (0.04–0.18 mM)’ (June hypolimnion), and more anaerobes were tied to ‘high Fe (>0.18 mM)’ (October hypolimnion).

The microbial iron redox cycle likely plays an important role in the seasonal Pu biogeochemical cycle. We previously modified the PICRUST2 (Douglas et al., 2020) database with functions involved in the microbial iron redox cycle (https://github.com/LLNL/2022_PondB_microbiome) and demonstrated that iron reduction and magnetosome formation were within the top 5% of pathways associated with stratification. The presence of iron and iron/sulfate reducers (Figure 16) suggests that the increased Pu observed in the hypolimnion could be derived from the biodissolution of iron minerals and particulate organic matter in the water column and sediments.

Table 3. Concentration ranges and statistics for ^{239}Pu distribution in R-canal and Pond B sediments.

# of samples (in triplicate)	50
Lowest Pu Concentration (mBq/kg)	0.01
Highest Pu Concentration (mBq/kg)	46.70
Mean Pu Concentration (mBq/kg)	4.02
Geometric mean Pu Concentration (mBq/kg)	1.46

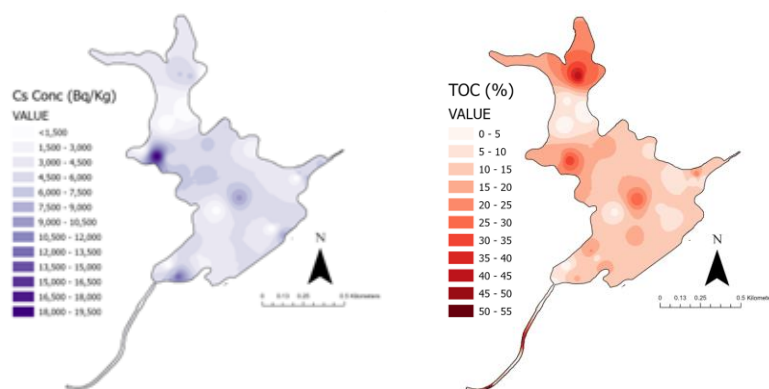


Figure 14. GIS maps of ^{137}Cs and Sediment Organic Carbon concentrations extrapolated from the 50 samples collected in FY22-FY23.

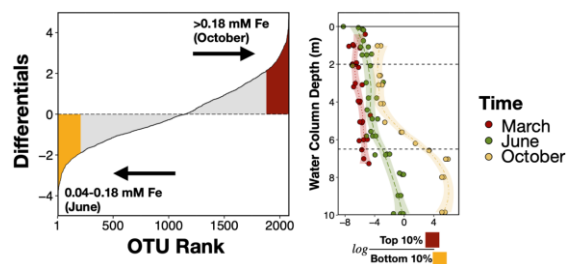


Figure 15. Differential OTU ranks of the Pond B water column microbiome by iron. The Pond B water column microbiome was ranked using Songbird in association with ‘high Fe’ (>0.18 mM; hypolimnion in October) and ‘mid Fe’ (0.04–0.18 mM; hypolimnion in June). The difference between the OTU rankings according to the top (red) and bottom (orange) 10% identified OTUs that varied between June and October hypolimnetic microbial communities.

We also determined that iron oxidizers and reducers have specific ecological niches within the Pond B water column (Figure 16). For example, the putative iron oxidizer *Ferrovum* was more abundant at ~3–5 m, and the iron oxidizer/reducer *Rhodoferrax* was more abundant near the transition between the thermocline and hypolimnion. Iron oxidizers can impact the Pu cycle through the formation of iron oxides that can sorb plutonium and particulate organic matter. In particular, *Ferrovum* plays a key role in the formation of iron-rich aggregates in other lakes, likely because of extracellular polysaccharide substance (EPS) production and encrustation of cells with Fe(III) precipitates. In Pond B, iron-encrusted microbial cells and EPS may act as sorption sites for plutonium.

From the microbial community results, we conducted microcosm studies in FY21–FY22 to evaluate the role of iron oxidizers and reducers on metal cycling using iron isotope ratios. 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). In FY22, we interrogated the magnitude of Fe isotope fractionation due to microbial reduction and oxidation using microcosms inoculated with anoxic and oxygenated water from Pond B. Fe isotopic fractionation data analysis is currently underway. We are also collaborating with Dr. Clara Chan, who is an expert on iron oxidizers and was awarded a DOE ESS proposal (see Synergistic Efforts section). Taken together with the Fe isotope microcosm studies, we hope to gain insight into the microbial iron cycle in Pond B.

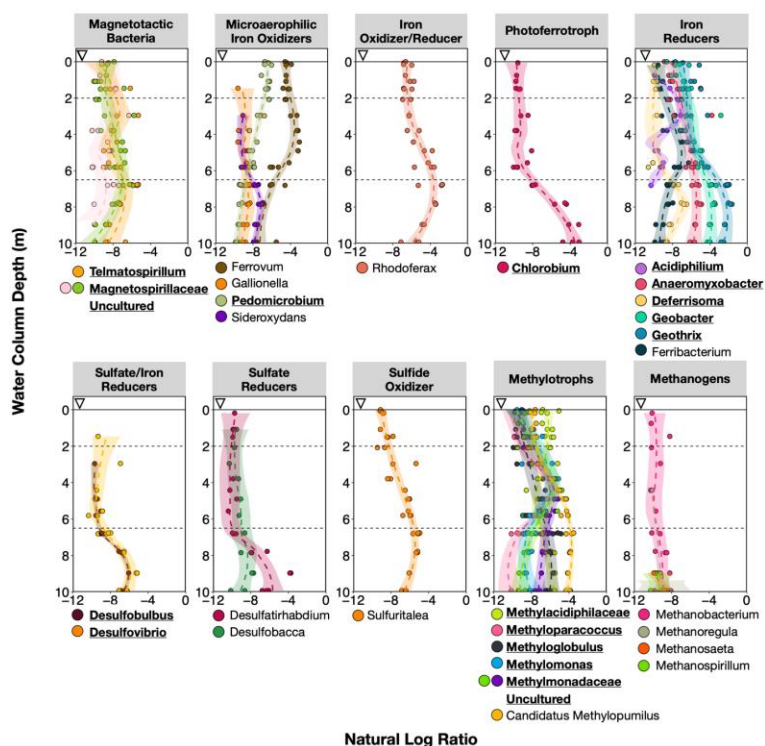


Figure 16. Water column profiles of specific taxa according to putative metabolic function. Bolded and underlined taxa were highly ranked (top 10%) differentially abundant OTUs associated with stratification compared to spring turnover.

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

Lead: B. Powell, **contributors:** D. Kaplan

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 $\text{Pu}^{\text{III}}_2(\text{C}_2\text{O}_4)_3(\text{s})$, PuO_2 nanocolloids, $\text{Pu}^{\text{V}}(\text{NH}_4)(\text{CO}_3)(\text{s})$ (with and without organic matter amended to the soil), and $\text{Pu}^{\text{IV}}(\text{C}_2\text{O}_4)_2(\text{s})$. In FY21 Pu sources from five of the lysimeters were collected and will be analyzed using XAS, XPS, and microscopy. Data will be compared to data previously collected four years ago (Maloubier et al., 2020). This new set of samples were in the field for 8 years.

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

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

LLNL SFA OBER—ESS FY23 Program Management and Performance Report: BioGeoChemistry at Interfaces 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 minerals 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., 1985). However, this is likely to oversimplify processes occurring in the environment. For example, Pu has a strong sorption affinity for Fe oxide minerals (Sanchez et al., 1985; Zhao et al., 2016) but Fe minerals in dynamic biogeochemical settings will likely be subject to dissolution and recrystallization (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 are two tasks associated with Focus Area 2A. Task 2A-1, initiated in FY19, focuses on Pu coprecipitation with Fe-oxides and calcite, and was completed in FY21. Task 2A-2 was intended to explore the formation of actinide-Al solution complexes 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 coprecipitation 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 and demonstrated 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 (Balboni et al., 2020). The results provided 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 behavior of Pu with calcite (CaCO_3). 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 XAS 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 this work were published in FY21 (Balboni et al., 2021).

Focus Area 2B: Actinide aging on mineral surfaces

Lead: E. Balboni, contributors: N. Wasserman, K. Morrison, K. Smith

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 two 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 FY20 (Pan et al., 2021). Task 2B-3 (Isotopic fractionation of Pu during sorption) was planned for FY20 but was delayed to FY22 due to COVID. 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 of Pu during sorption

Similar to other heavy metals, Pu isotopes have the potential to undergo mass-dependent and mass-independent fractionation. Reactions such as adsorption/desorption and redox transformations are known to fractionate uranium (U) isotopes through the nuclear volume effect (Brennecke et al., 2010; Stirling et al., 2007). Previous studies have leveraged U isotope ratios to shed light on U fate and transport in contaminated sites (Brown et al., 2018; Jemison et al., 2020) and comparable applications are also possible for Pu isotopes, which are close to U in mass. To determine the effects of sorption and redox reactions to the fractionation of Pu isotopes, we set up a series of batch sorption experiments where Pu was reacted with montmorillonite: 1) SWy-2 montmorillonite characterized by ~3% Fe wt. At the beginning of FY22 we performed the first batch sorption experiments with SWy-2. Previous studies (Begg et al., 2018) and batch experiments with ^{238}Pu indicate that Pu(IV) equilibration with SWy-2 montmorillonite occurs on the order of hours. In our experiments a well-characterized Pu standard (CRM 137 doped with CRM 130) was equilibrated at an initial Pu concentration of $\sim 5 \times 10^{-10}\text{M}$ in a synthetic groundwater at pH 8.0. Suspensions of SWy-2 were equilibrated with the Pu-doped synthetic groundwater to create a 0.2 g/L suspension. The suspensions were sampled at various timepoints (T=0, 24 hours, 1 week, 1 month, 3 months, and 6 months) for Pu for isotopic analysis. Solid samples were purified and measured twice on the Nu Plasma HR and the Nu Plasma 3 MC-ICPMS. The liquid samples were measured once on the Nu Plasma 3 MC-ICPMS. While the liquid samples were on average isotopically heavier than the solid samples, the analytical uncertainty of our measurements, or twice the standard error of replicate analyses, was larger than the difference between liquid-solid in a single timepoint. As the number of replicate analyses was limited by Pu mass present in each fraction, greater Pu mass in larger volume experiments are needed to explore the fractionation of Pu isotopes during sorption.

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

Lead: Y. Jiao, contributors: N. Merino

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 FY23, we continued to evaluate the sorption of Pu to microbial cells to provide insights into Pu immobilization onto microbial communities enriched from SRS Pond B.

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 previously conducted microcosm experiments to enrich for specific metabolisms present in Pond B. The exudates work was ramped down in preparation for the new science research plan with ANL. Instead, we focused on Pu partitioning to microbial cells in SRS Pond B waters (Figure 17). The cells were added to Pond B water (filtered through 0.2 μm to remove natural cells) at varying cell concentrations, and we found that Pu sorption followed similar trends for all types of microbial communities enriched. At least 10^5 – 10^6 cells/mL are required to effectively sorb Pu. For comparison, the *in-situ* cell concentrations in Pond B water are on average about 10^5 cells/mL. The least sorptive cells were those derived from the algal enrichment condition while bacterial cells tended to have similar sorption affinities. Pu sorption affinities (Figure 17) follow a trend with cell density. As cell density decreases, the sorption affinity (K_d) increases, demonstrating that microbial cells are an important factor in Pu immobilization at cell concentrations typical of environmental systems. It also indicates that Pu affinity estimates measured at high cell densities may drastically underestimate the affinity of Pu for cell surfaces. This underestimate is likely the result of cell aggregation leading to much lower apparent cell surface concentrations. This trend also seems to be corroborated by other studies and suggests that cell type (i.e., fungal, algal, bacterial) may not impact Pu sorption.

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

The goal of Task 2C-2 and Task 2C-3 is to determine the ability of microbial exudates to mobilize Pu from mineral surfaces. These two tasks were ramped down in preparation for the new science research plan with ANL (SFA3).

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 (Figure 16), likely based on the surrounding biogeochemical conditions, such as dissolved oxygen. This task is being ramped down in preparation for the new science research plan with ANL (SFA3).

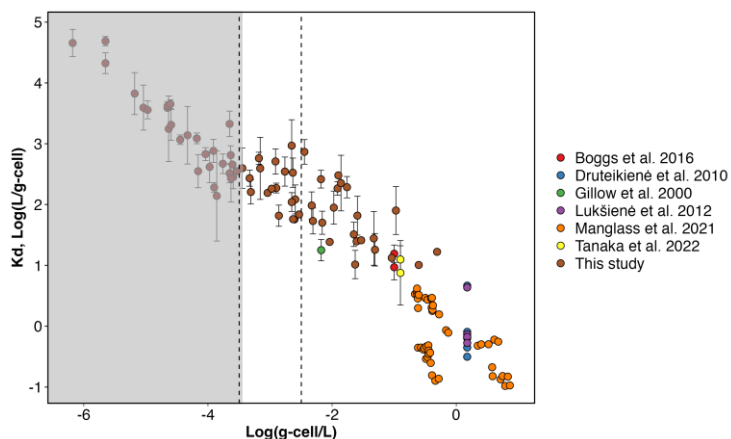


Figure 17. Pu(IV) sorption affinity by cell densities. The two vertical dotted lines represent the minimum and maximum weight of cells in Pond B, estimated from cell concentration (cells/mL). The gray box indicates the samples affected by experimental abiotic factors. Error bars represent the standard deviation of experimental replicates (n = 3–7).

4.a.ii and iii Science Highlights and Publications Statistics

Scientific Highlights

Of the 11 peer-reviewed manuscripts (**with a total of 70 co-authors**) completed during this review period (and one book chapter), 7 have been published, three are accepted, and one has been submitted and is undergoing review. 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 (Table 4). In addition to our journal publications, we published one book chapter, chaired four sessions at multiple conferences, presented 19 talks or posters at national and international meetings and universities, including 9 invited presentations, and published two datasets on the ESS-DIVE platform.

Table 4. Publication Statistics.

Journal	Pubs	Impact Factor
Env. Sci. & Tech.	1	11.4
Sci. Total Environ.	2	11.0
J. Coll. Interf. Sci.	1	10.0
Chemosphere	1	8.9
Env. Res. Letters	1	6.8
Nature Sci. Repts.	2*	5.0
Appl. Geochem.	3	3.8

* includes submitted manuscript

Publications (2022-2023)

1. Merino, N., Wasserman, N.L., Coutelot, F., Kaplan, D., Powell, B., Jiao, Y., Kersting, A.B., Zavarin, M. *Submitted*. Microbial community dynamics impact plutonium and iron biogeochemical cycles in a seasonally stratified pond, *Nature Sci. Reports*.
2. Chang, E., Zavarin, M., Beverly, L., and Wainwright, H. *Accepted*. A chemistry-informed hybrid machine learning approach to predict metal adsorption onto mineral surfaces, *Appl. Geochem*.
3. Wasserman, N.L., Merino, N., Coutelot, F., Powell, B.A., Kersting, A.B., and Zavarin, M. *Accepted*. Seasonal and long-term cycling of plutonium in a monomictic pond. *Nat. Sci. Repts*.
4. Han, S-C., Chang, E., Zechel, S., Bok, F., and Zavarin, M. *Accepted*. Application of community data to surface complexation modeling framework development: Iron oxide protolysis, *J. Coll. Interf. Sci*.

5. Chang, E. Beverly, L., and Wainwright, H. 2023. Constrained Autonomous Modeling of Metal-Mineral Adsorption, In *Methods and Applications of Autonomous Experimentation*, Marcus Michael Noack and Daniela Ushizima, Eds.
6. Coutelot, F., Wheeler, J., Merino, N., Kaplan, D.I., Owings, S., Tallefert, M., Zavarin, M., Kersting, A.B., Powell, B.A. 2023. Temporal evolution of Pu and Cs sediment contamination in a seasonally stratified pond, *Sci. Tot. Env.*, <https://doi.org/10.1016/j.scitotenv.2022.159320>.
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11. 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. 2022. From legacy contamination to watershed systems science: A review of scientific insights and technologies developed through DOE-supported research in water and energy security, *Env. Res. Lett.*, <https://doi.org/10.1088/1748-9326/ac59a9>
12. Zavarin, M., Chang, E., Wainwright, H., Parham, N., Kaukuntla, R., Zouabe, J., Deinhart, A., Genetti, V., Shipman, S., Bok, F., and Brendler, V. 2022. A Community Data Mining Approach for Surface Complexation Database Development, *Env. Sci. Technol.* 56 (4), 2827-2838. <https://doi.org/10.1021/acs.est.1c07109>

Datasets (2022-2023)

1. Han S ; Chang E ; Zechel S ; Bok F ; Zavarin M (2023): Community Based Data of Potentiometric Titration of Iron Oxides: Ferrihydrite (HFO), Goethite, Hematite, Magnetite. Subsurface Biogeochemistry of Actinides SFA, ESS-DIVE repository. Dataset. [doi:10.15485/1986089](https://doi.org/10.15485/1986089) accessed via <https://data.ess-dive.lbl.gov/datasets/doi:10.15485/1986089> on 2023-06-22
2. Zavarin M ; Chang E ; Wainwright H ; Parham N ; Kaukuntla R ; Zouabe J ; Deinhart A ; Genetti V ; Shipman S ; Bok F ; Brendler V (2022): Community Based Data of Uranium Adsorption onto Quartz. Subsurface Biogeochemistry of Actinides SFA, ESS-DIVE repository. Dataset. [doi:10.15485/1880687](https://doi.org/10.15485/1880687) accessed via <https://data.ess-dive.lbl.gov/datasets/doi:10.15485/1880687> on 2023-06-22

4.B FUTURE SCIENTIFIC GOALS, VISION AND PLANS

While our SFA remains focused on completing our original planned tasks and efforts to elucidate the BioGeoChemistry at Interfaces as it relates to actinides, redox sensitive metals, organic matter, and microbial community function and composition, we spent a significant time in FY23 developing a new SFA program in terrestrial wetlands research. We focused on future goals, vision, and plans that are aligned with the research goals of the Environmental System Science (ESS) program within BER to advance a robust, predictive understanding of how watersheds function as integrated hydro-biogeochemical systems, as well as how these systems respond to disturbances such as changes in water recharge, availability, and quantity; contaminant release and transport; nutrient loading; land use; and vegetative cover. These discussions were coordinated with our SFA partners at Argonne National Laboratory and were intended to provide a unified vision for a coordinated LLNL-ANL SFA program. Our discussions with our ANL partners and EESS program management led to the development of a white paper entitled “Terrestrial Wetland Function and Resilience Scientific Focus Area” that outlines our SFA scientific goals, vision, and plans for the future (Figure 18). The White Paper was delivered to BER on October 17, 2022.

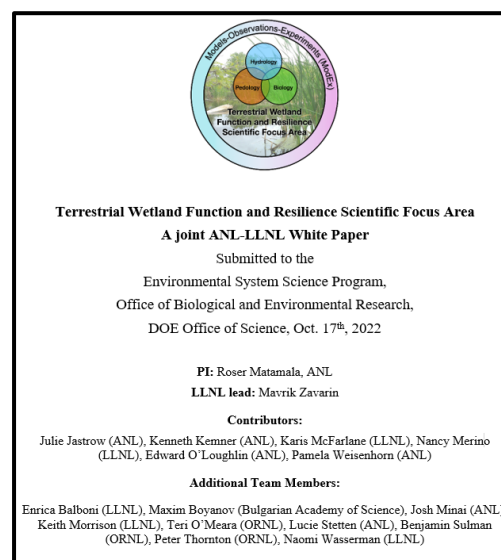


Figure 18. The ANL-LLNL terrestrial wetland SFA white paper.

4.C NEW SCIENTIFIC RESULTS

New Scientific Results	Identified Gaps in Knowledge for Future Investigation
Identified how the dynamics of microbial community composition, both spatial and temporal, in stratified ponds drives metal cycling.	How do these same biogeochemical processes impact C cycling in transient redox systems such as terrestrial wetlands?
Data/modeling workflows can harness community geochemical data and parameterize processes using traditional and hybrid ML approaches.	Can these same “big data” and hybrid ML approaches yield a process level understanding of mineral associated soil organic matter and its cycling in soils?
Contaminants may become less susceptible to mobilization as a result of long term (decadal) aging in the environment.	How do we understand the processes controlling the aging phenomenon and can it be attributed to mineral weathering?
Organic chelators can drastically enhance the mobility of metals and radionuclides in the environment.	A paradigm shift is required to dramatically improve organic matter compound characterization in soils and sediments, determine their stability with respect to C cycling, and quantify their impact to metal cycling.

4.D COLLABORATIVE RESEARCH ACTIVITIES

We currently have 8 collaborations, two of which have been funded through subcontracts.

Brian Powell—Professor at Clemson University. We have a long-standing collaboration with Dr. Powell. Dr. Powell is subcontracted to lead 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. He mentors graduate students and one postdoc and is responsible for managing our field effort at Pond B, SRNL. We plan to extend funding to Clemson in FY24 to support completion of efforts at SRS Pond B.

Dan Kaplan (SRNL) has deep insight into the history of Pond B and is providing support with coordinating field work at that site. Dr. Kaplan received a subcontract of 50K from LLNL in FY22 that was completed in FY23 to support field activities at Pond B.

Dr. Gareth Law (U. of Helsinki and previously at Manchester University) helped to wrap up our efforts at the Ravenglass estuary, Focus Area 1B.

Nathalie Wall (Univ. of Florida) and her graduate student (Emily Maulden) are supporting our efforts at the Hanford site. These efforts will be completed in late FY23.

Carolyn Pierce (PNNL) is supported through PNNL's environmental management program and (with Hillary Emerson) providing guidance for our efforts at the Hanford site. These efforts will be completed in late FY23.

Sol-Chan Han (Postdoc Korea Advanced Institute of Science & Technology) was initially supported through a Korean fellowship before transitioning to a LLNL postdoc position and is helping develop a computational framework for surface complexation modeling based on community data from the L-SCIE database. This effort is aligned with AI4ESP seed funding received in FY22.

Clara Chan (University of Delaware) is a geomicrobiologist whose research explores the evolution of life and how microbes affect environmental chemistry. She has been collaborating with us to investigate the microbial iron redox microbes at Pond B, Savannah River, S.C. using metagenomics. Overall, Dr. Chan's work integrates with this SFA's research objective to understand the role of Fe(II)/Fe(III) cycling on actinide mobility.

AI4ESP Project: As part of our AI4ESP seed funding, significant effort has been applied to developing sorption prediction workflows. The tasks include development of community data-driven surface complexation modeling frameworks, hybrid ML workflows, and community database development. The collaboration with Dr. Wainwright (MIT), who is a DOE Management Core Team staff for the AI4ESP initiative, has provided key directions and support for the LLNL team to develop new modeling approaches that integrate uncertainty quantification and error propagation. We anticipate that the approaches in development as part of this AI4ESP seed project will be incorporated into our process modeling framework for C cycling in our proposed Terrestrial Wetland SFA.

In FY23, significant effort has been placed in developing sorption prediction workflows based on community sorption data. The tasks include development of (1) a workflow utilizing a traditional surface complexation modeling approach for simulating potentiometric titration of mineral surfaces and radionuclide sorption, and (2) a machine learning based sorption prediction workflow. Through the efforts in FY23, we have published one journal paper (Han et al., 2023) and one book chapter (Chang et al., 2023), and submitted a manuscript, which was just accepted in Applied Geochemistry (Chang et al., Accepted). These three manuscripts were preceded by a manuscript that outlined the FAIR community data approach (Zavarin et al., 2022).

The first FY23 study started with the aim of constructing a self-consistent surface complexation model (SCM) database. Although numerous studies have shed light on surface complexation modeling, it was found that there was an impasse in the integration of data scattered in different studies and in obtaining a consensus among those studies. Different SCM constraints have been reported even in the case when the same sorption systems were under investigation. This fact leads to ambiguity in the selection of 'representative' SCM constants and in the further development of self-consistent surface complexation databases. In other words, it was required to develop a comprehensive SCM framework, which can reconcile the full community-wide data, in order to produce 'representative' reaction constants to be utilized in downstream sorption modeling. In light of this challenge, we proceeded to integrate, and model digitized and compiled potentiometric titration data, reported following the Findable, Accessible, Interoperable, Reusable (FAIR) data principles (Wilkinson et al., 2016). The surface complexation modeling focuses on fitting compiled community data for each individual iron oxide mineral (i.e., ferrihydrite, goethite, hematite, and magnetite) to produce representative protolysis constants, which are essential input parameters for sorption modeling. Using the developed workflow, the impact of SCM type and surface site density (SSD) on the fit quality and protolysis constants can be readily evaluated. By providing the most appropriate protolysis constants (and associated parameter uncertainties), this study provides improved constraints to be utilized in downstream SCM development. This work was performed in collaboration with Frank Bok and Susanne Zechel (Helmholtz-Zentrum Dresden-Rossendorf, Germany) and published in Journal of Colloid and

LLNL SFA OBER—ESS FY23 Program Management and Performance Report: BioGeoChemistry at Interfaces Interface Science (Han et al., 2023). A follow-on task of community data-driven surface complexation modeling for selenium sorption onto iron oxides is currently underway.

The second FY23 study was aimed at developing sorption prediction workflow by utilizing machine learning (ML) instead of traditional surface complexation modeling approach. At its core, the workflow was motivated by the proliferation of incongruent SCMs in the literature that limit their applicability in reactive transport models. The developed workflow, so called hybrid ML approach, exploits thermodynamic aqueous speciation calculations while replacing the SCM interfacial chemical modeling with a data-driven, random forest (RF)-ML approach. The values from aqueous speciation simulations are automatically used as input features for a RF algorithm to quantify adsorption. By doing so, we develop a new model that is not hindered by limitations of explicit surface descriptions: we eliminate challenges associated with assumptions on electrostatic surface effects and complicated permutations of relevant reaction stoichiometries that potentially convolute overall mechanism. The developed workflow has yielded successful predictions of U(VI) adsorption onto quartz and montmorillonite mineral surfaces, while suggesting distinct sorption processes of surface complexation and ion-exchange. This work has been done in collaboration with Haruko Wainwright (MIT) and recently accepted in Applied Geochemistry (Chang et al., Accepted). A similar workflow that utilized Gaussian process was published as a book chapter (Chang et al., 2023).

AI4ESP student training workshop: With the significant progress made on the community-based data assimilation and processing workflows (efforts encompassed by the AI4ESP work described above), the LLNL modeling team coordinated a week-long, in-person engagement with Dr. Powell (Clemson University) in June, 2022. LLNL trained Clemson University staff on how to implement our latest community data and modeling work packages. This training engaged undergraduate students to execute the work packages and detect areas for improvement. Ultimately, this week-long interaction has prepared the LLNL modeling team to hold an interactive workshop at an upcoming conference (to be determined) in order to disseminate the latest modeling tools to the broader scientific community.

Synergistic proposals and projects:

- **Vulnerability Assessment of Soil and Groundwater Contamination near Zaporizhzhia NPP, Ukraine using the DRASTIC Model:** With support from the LDRD offices at LLNL and LBNL, a team of scientists from the two national laboratories examined the risks of radiologic contamination to groundwater near the Zaporizhzhia nuclear power plant in Ukraine.
- **WDTs Outreach Consortium of Livermore Institutes and Centers:** With support from the DOE Office of Science and the new University of California Livermore Collaboration Center, LLNL hosted a two-day workshop that included 17 Minority Serving Institutions and highlighting the workforce development missions of LLNL's twelve Institutes and Centers (August 3 and 4, 2022).
- **AI4ESP Seed proposal:** AI-enabled assimilation of community geochemical datasets into reactive transport models, Co-PIs: Haruko Wainwright, Elliot Chang, Sergi Molins, Marcus Noack and Mavrik Zavarin, 300K (100K subcontract to LLNL). This effort was extended into FY23.
- **Stockpile Stewardship Academic Alliance proposal:** Combined Field and Laboratory Studies of Plutonium Aging and Environmental Transport, PI: Brian Powell (funded)

4.E DATA MANAGEMENT

We are committed to the open sharing of LLNL SFA documentation consistent 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 et al., 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

LLNL SFA OBER—ESS FY23 Program Management and Performance Report: BioGeoChemistry at Interfaces 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. Two datasets were recently loaded onto the ESS-Dive archive (see 4.a.ii and iii).

5. STAFFING AND BUDGET SUMMARY

5.A FUNDING ALLOCATION BY PROGRAM ELEMENT

5.a.i Present Funding

5.a.ii Funding Changes

In FY24, we plan to extend a subcontract to Clemson University to complete field sampling and analysis and publication preparation associated with our SRS Pond B focus area. We are planning for this effort to wind down in FY24.

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. 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. This effort will be winding down in FY24.

5.b.ii National Laboratories

A SRNL subcontract was carried over from FY22. This funding supported Dan Kaplan's assistance in field sampling and permitting at the SRS. One subcontract was initiated from ANL to LLNL in support of planning and equipment purchases for the Terrestrial Wetland SFA.

5.C PERSONNEL ACTIONS

5.c.i. New Hires



Nancy Merino was converted from postdoc to staff scientist in June, 2022. Nancy is playing a critical role in developing the Terrestrial Wetland SFA research program. Nancy will be leading LLNL's effort in microbiome research and GIS analysis as part of the proposed new SFA.



Teresa Baumer was converted from postdoc to staff scientist in November, 2022. Teresa joined the analytical chemistry group where she will continue to support the analytical chemistry needs of this SFA.

Jon Golla just accepted a postdoc position at LLNL (start date August 28, 2023). He will be conducting geospatial analyses, spatial statistics, and biogeochemical modeling in preparation for the Terrestrial Wetlands SFA. Jon will be evaluating climate change impacts on terrestrial wetlands within the contiguous United States by using geospatial information systems (GIS) and reactive transport models (RTMs). Jon has extensive experience modifying RTMs, including the source code for CrunchFlow/CrunchTope. Jon is currently completing his PhD at the University of Illinois at Urbana-Champaign, where he is using lithium isotopes with geochemical data and RTMs to investigate stream flow and hydrological perturbations.

5.c.ii. Anticipated Future Hires

We are hiring two new postdocs in preparation of our transition to a Terrestrial Wetland SFA research program, and we are in the process of converting Naomi Wasserman from postdoc to a staff scientist. As our SFA program is shifting toward a more wetlands science research program, we are envisioning a need for support in the areas of numerical modeling (Jon Golla) and organic chemistry (TBD).

We have completed the first round of interviews for the organic mass spectrometry postdoc position. The candidate will advance our understanding of organic matter cycling in wetland environments by developing GC-MS, LC-MS, and other techniques to characterize the composition of natural organic matter and other complex mixtures of organic compounds. This will be achieved through various extractions using columns and dialysis along with derivatization of compounds that traditionally escape GC and LC-MS detection. The new postdoc will utilize the new organic matter research laboratory at LLNL that was recently established to support future SFA research.

5.c.iii. Releases



Elliot Chang was hired as a new postdoc in late 2021 to lead modeling efforts that incorporate new machine learning techniques into traditional surface complexation and reactive transport modeling. He has been involved in numerous external strategic projects as well, such as the AI4ESP synergistic project. Elliot received his PhD from U.C. Berkeley, where he modeled rare earth element mobility and sorption processes in engineered bioreactors and natural soil systems. Elliot left LLNL in 2023 to pursue a career in enhanced rock weathering in the private sector.



Annie Kersting retired in April, 2023. Annie played a critical role in the establishment of the original biogeochemistry SFA at LLNL (originally titled the Plutonium BioGeoChemistry SFA). Annie continues to support the program as a visiting scholar. However, she is stepping down from the leadership position as the SFA transitions to a focus in Terrestrial Wetlands research.

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 had 9 students participate in our SFA: 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 and SULI programs 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. Nine students were involved in the SFA and synergistic projects. **1. Jordan Graham**, 2023 summer intern – Norfolk State University (organic matter characterization), **2. Liuba Williams**, 2023 summer intern – University of Nevada Las Vegas (Sorption and Community database development), **3. Zachary Murphy**, 2023 summer intern – University of Central Florida (actinide-OM complexation), **4. Russell Cox**, 2022 spring SULI student– University of Central Florida (Pu-TBP complexation), **5. Gardner Campbell**, 2022 summer MARA student – (ML applications to geochemistry), **6. Linda Beverly**, 2022 summer student – Cal State East Bay (community database development for geochemistry), **7. Jordan Stanberry**, 2022 summer student – University of Central Florida (soil characterization of ephemeral ponds at NNSS), **8. Suzan Aranda**, 2022 summer student – University of Texas at El Paso (GIS meta analysis of US terrestrial wetlands), **9. Jenna Bustos**, 2022 summer student – Oregon State University (actinide-OM complexation)

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). This includes a mini-sabbatical for Frank Yang (University of Nevada, Reno) to develop research collaborations in organic matter-mineral-bacteria interfacial redox reactions. This research will be relevant to our efforts in Terrestrial Wetland research.

LLNL has purchased an elemental analyzer for the analysis of CHNOS in solid samples for carbon cycle research. The Elementar EL Cube elemental analyzer offers simultaneous analysis of CHNS in a single sample, with masses ranging from μg to gram quantities of samples. This offers an extremely adaptable sample system that allow rapid analysis of bulk soils and organic extracts. In addition to the thermal conductivity detector, the system is also equipped with high sensitivity infrared and electrochemical cells for the detection of trace S and O. The addition of high throughput elemental analysis will serve as the starting point for organic matter characterization and guide more advanced mass spectrometry based techniques.

5.d.i. Staffing & Expertise Needs

See 5.c.ii

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

With SFA3 seed funding, we purchased a Elementar Vario Cube TIC/TOC (total organic carbon/total inorganic carbon) analyzer. This instrument can measure the total organic carbon of solid and liquid samples in a variety of matrices and is optimized to deal with compounds hard to oxidize, such as humic acids or other persistent compounds. In addition, the vario TOC cube is one of the very few analyzers on the market that allows measurement of solid and liquid samples with a single instrument – mode switching is done within minutes. The instrument arrived at LLNL in May 2023 and is scheduled for installation for September 2023.

Organic Matter Research Lab (OMRL): Our group recently acquired a new laboratory space for the characterization of organic matter using mass spectrometry. This lab space is equipped with 4 chemical fume hoods, centrifuges, rotovap, solid phase micro-extraction, nitrogen purge heating blocks, scales and a micro balance. The lab has 3 GC-MS systems, one LC-MS and an elemental analyzer for CHNOS analysis of solid samples. LLNL is supporting the update of this space to allow for the development of a unique organic matter characterization facility focused on high throughput soil organic carbon characterization.

The new ORML is a multi-approach facility for characterizing complex natural organic matter in complex soil environments, with a range of mass spectrometry and elemental analysis techniques. The facility offers multiple

derivatization techniques for GC-MS and LC-MS analysis, including techniques that allow for both untargeted and targeted analysis of soil microbial metabolites, lipids, amino acids, lignin, and proteins. The MS/MS configuration of all of the mass spectrometers allows extremely low detection levels (femtogram) of targeted analytes in a complex organic matrix, giving the ability to track specific isotopically labeled compounds at trace levels. Pyrolysis GC-MS with cryo-trapping facilitates analysis of solid and mineral bound organic fractions that elude many other analytical techniques. *In-situ* pyGC-MS derivatization techniques provide a rapid high-throughput approach for screening soil organic matter, microbial and plant lipids via fatty acid methyl acids. These techniques are coupled to CHNOS elemental analysis of solids along with total organic and inorganic carbon analysis to determine how organic matter composition and quality coupled to mineral, microbial and plant re-processing shape stable pools of organics. The analysis of volatile organic compounds (VOCs) can be explored using SPME-GC-MS/MS, and eventually, a real time SIFT-MS VOC analyzer. Monitoring of soil VOCs can be used as a tool to track microbial metabolic processes and cell signaling coupled to organic matter availability and stability. High-throughput analysis of soil DOM can be measured with fluorescence EEM analysis and the results processed with parallel factor analysis to determine organic matter sources and the degree of macromolecular structure associated with different soil environments. Also possible are cutting edge particle extraction techniques (SPLITT fractionation) to rapidly separate gram quantities of particles from the 100's of micron range down to colloidal sizes. This separation pipeline is coupled to a suite of mineral characterization techniques to measure mineralogy (qXRD), particle size and surface charge (Zetasizer), surface area (BET) and the organic mass spectrometry techniques mentioned above. Together, these techniques allow us to discern processes that lead to the formation of stable microbe-mineral-organic micro aggregates and the formation of stable organic carbon soil pools.

5.E CAPITAL EQUIPMENT NEEDS

Capital equipment needs are anticipated for this SFA as we build our vision for a new focus on terrestrial wetland research. We recently upgraded our laboratory with an Elementar TIC/TOC groundwater analysis instrument using the terrestrial wetland startup funding subcontract from ANL. In addition, recent capital equipment purchases made with the support from this SFA and internal LLNL investments include an Agilent 8890 GC System, Edinburgh Instruments FLS1000 steady state and lifetime TCSPC fluorimeter, and hybrid Senterra II[®] confocal Raman imaging microscope. Nevertheless, we anticipate that additional capital equipment will be needed. SIFT-MS is an exceptional technique that would allow for real time VOC analysis in soil microcosm and field soil C flux studies. State-of-the-art Orbitrap MS (ThermoScientific ECLIPSE MS) plays an essential role in organic matter characterization and access to this technology is limited at LLNL. Indeed, both instruments can play a critical role in organic matter characterization for a number of BER SFAs at LLNL, including the proposed Terrestrial Wetland SFA.

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