

## **Title: The LLNL Biogeochemistry at Interfaces SFA**

Mavrik Zavarin,<sup>1\*</sup> Annie Kersting,<sup>1</sup> Enrica Balboni,<sup>1</sup> Teresa Baumer,<sup>1</sup> Gauthier Deblonde,<sup>1</sup> Yongqin Jiao,<sup>1</sup> Harris Mason,<sup>1</sup> Nancy Merino,<sup>1</sup> Keith Morrison,<sup>1</sup> Chao Pan,<sup>1</sup> Naomi Wasserman,<sup>1</sup> P.Todd Woody,<sup>1</sup> Keenan Thomas,<sup>1</sup> Brian Powell,<sup>2</sup> Fanny Coutelot,<sup>2</sup> Jessie Wheeler,<sup>2</sup> Corwin Booth,<sup>3</sup> Kurt Smith,<sup>3</sup> Gareth Law,<sup>4</sup> Dan Kaplan,<sup>5</sup> Nathalie Wall,<sup>6</sup> Emily Maulden,<sup>6</sup> Vickie Freedman,<sup>7</sup> Carolyn Pearce,<sup>7</sup> K. Cantrell,<sup>7</sup> and Hilary Emerson<sup>7</sup>

<sup>1</sup>Lawrence Livermore National Laboratory, Livermore, CA; <sup>2</sup>Clemson University, Clemson, SC; <sup>3</sup>Lawrence Berkeley National Laboratory, Berkeley, CA; and <sup>4</sup>University of Helsinki, Finland; <sup>5</sup>Savannah River National Laboratory, Aiken, SC; <sup>6</sup>University of Florida, Gainesville, FL; <sup>7</sup>Pacific Northwest National Laboratory, Hanford, WA

**Contact:** ([zavarin1@llnl.gov](mailto:zavarin1@llnl.gov))

**Project Lead Principal Investigator (PI):** Mavrik Zavarin

**BER Program:** ESS

**Project:** LLNL DOE SFA: Biogeochemistry at Interfaces

**Project Website:** [https://doesbr.org/research/sfa/sfa\\_llnl.shtml](https://doesbr.org/research/sfa/sfa_llnl.shtml)

**Project Abstract:** The focus of the BioGeoChemistry at Interfaces SFA is to identify and quantify the biogeochemical processes and the underlying mechanisms that control actinide and metal ion mobility to reliably predict their cycling and migration in the environment. The research approach includes: (1) Field studies that capture behavior on the timescale of decades and (2) Fundamental laboratory studies that isolate specific biogeochemical processes observed in the field. These efforts 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 and metal ion behavior in the environment, and serve as an international resource for environmental science and radiochemistry research.

Despite the challenges of the past year, our team has maintained its scientific productivity (10 manuscripts published/submitted), established a new ephemeral stream Test Bed at the Nevada National Security Site, hired two new postdocs (Naomi Wasserman and Teresa Baumer), and initiated a new focus area in machine learning in geochemistry. Exciting scientific results of the past year include 1) discovering how bacterial surfaces can facilitate the precipitation of U-phosphate minerals by providing a local environment that is supersaturated with respect to U-phosphate minerals (Morrison et al., 2021), 2) identifying how reducing conditions can lead to Fe and Pu mobilization in estuaries, 3) identifying the enhanced Fenton-type oxidation potential of surface water and shallow sediments in the presence of organic matter (Pan et al., 2021), and 4) identifying how subsurface planktonic microbial communities reflect regional-scale groundwater hydraulic connectivity and groundwater flow patterns (Merino et al., submitted).

### **References**

Morrison, K.D., Zavarin, M., Kersting, A.B., Begg, J., Mason, H.E., Balboni, E., & Jiao, Y. (2021) The influence of uranium concentration and pH on U-phosphate biomineralization

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<sup>2</sup>Pan, C., Jiao, Y., Kersting, A.B., & Zavarin, M. (2021). Plutonium redox transformation in the presence of iron, organic matter and hydroxyl radicals: Kinetic and mechanistic insights, Environ. Sci. Technol. 55:1800-1810. <https://doi.org/10.1021/acs.est.0c08195>.

<sup>3</sup>Merino, N., Jackson, T.R., Campbell, J.H., Kersting, A.B., Sackett, J., Zavarin, M., Hamilton-Brehm, S.D., Moser, D.P. Subsurface planktonic microbial communities reflect regional-scale groundwater hydraulic connectivity, submitted to PNAS (2021).

**Title: BioGeoChemical Cycling at a Monomictic Stratified Pond, Savannah River Site, SC**

Brian A. Powell,<sup>1</sup> Nancy Merino,<sup>2</sup> Fanny Coutelot,<sup>1</sup> Naomi Wasserman,<sup>2</sup> Jessie Wheeler,<sup>1</sup> Yongqin Jiao,<sup>2</sup> and Daniel I. Kaplan,<sup>3</sup>, Mavrik Zavarin,<sup>2</sup> Annie B. Kersting<sup>2</sup>

<sup>1</sup>Clemson University, Clemson, SC; <sup>2</sup>Lawrence Livermore National Laboratory, Livermore, CA;

<sup>3</sup>Savannah River National Laboratory, Aiken, SC

**Contact:** ([zavarin1@llnl.gov](mailto:zavarin1@llnl.gov))

**Project Lead Principal Investigator (PI):** Mavrik Zavarin

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**Project:** LLNL DOE SFA: Biogeochemistry at Interfaces

**Project Website:** [https://doesbr.org/research/sfa/sfa\\_llnl.shtml](https://doesbr.org/research/sfa/sfa_llnl.shtml)

**Project Abstract:** Pond B at Savannah River Site (SRS) is an ideal location for examining the biogeochemical cycling of Fe, Pu, organic matter, and other metals in a monomictic stratified pond. This pond received reactor cooling water from 1961–1964 containing trace levels of <sup>238,239,240</sup>Pu, <sup>137</sup>Cs, <sup>90</sup>Sr, <sup>241</sup>Am, and <sup>244</sup>Cm. 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. However, the mechanism(s) causing Pu mobilization have not been identified.

During summer stratification, Pu, Fe and <sup>137</sup>Cs aqueous concentrations increase with depth, consistent with historical observations and likely linked to reductive dissolution of Fe-(oxy)hydroxides and mobilization of organic matter. These trends are consistent with 1983 measurements of <sup>239,240</sup>Pu activity in Pond B, although Pu concentrations have since decreased 2- to 3-fold in the water column and slightly in the soil profiles. Pu isotopic ratios fall between accepted values for Northern Hemisphere fallout and previously recorded ratios at SRS. This range most likely reflects the mixing between atmospheric sources of Pu and historical releases into Pond B. Comparisons of the concentration profiles within soil cores help explain metal cycling in the water column. Total <sup>239</sup>Pu and <sup>237</sup>Cs from the inlet, the bank and outlet of the pond, show that Pu and Cs accumulation is largely restricted to the upper 5 cm of sediment and appears highly correlated with organic matter.

We found that the Pond B water microbial community varies with depth rather than location during stratification and can be categorized by the three distinct stratification layers. However, during spring turnover, the microbiome is homogenized throughout Pond B, reflecting the uniform geochemistry (e.g., oxygen concentrations, temperature, metals). Further analysis of the microbial community is ongoing, including identifying co-occurring microbes and ontological predictions of metabolisms and functions. Future analysis will also include the development of a database of iron oxidizers and reducers for predicting microbial iron redox functions using 16S rRNA amplicon sequencing data.

**Title: LLNL SFA Test Beds at the Ravenglass Estuary (UK), Hanford Site Vadose Zone, and Nevada National Security Site Ephemeral Stream**

Mavrik Zavarin,<sup>1\*</sup> Annie Kersting,<sup>1</sup> Enrica Balboni,<sup>1</sup> Teresa Baumer,<sup>1</sup> Nancy Merino,<sup>1</sup> Naomi Wasserman,<sup>1</sup> Nathalie Wall,<sup>2</sup> Emily Maulden,<sup>2</sup> Carolyn Pearce,<sup>3</sup> K. Cantrell,<sup>3</sup> and Hilary Emerson<sup>3</sup>

<sup>1</sup>Lawrence Livermore National Laboratory, Livermore, CA; <sup>2</sup>University of Florida, Gainesville, FL;

<sup>3</sup>Pacific Northwest National Laboratory, Hanford, WA

**Contact:** ([zavarin1@llnl.gov](mailto:zavarin1@llnl.gov))

**Project Lead Principal Investigator (PI):** Mavrik Zavarin

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**Project Website:** [https://doesbr.org/research/sfa/sfa\\_llnl.shtml](https://doesbr.org/research/sfa/sfa_llnl.shtml)

**Project Abstract:** The BioGeoChemistry at Interfaces SFA includes four test beds and one engineered field site that 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. These test beds allow us to test our conceptual and mechanistic understanding of actinide migration using long-term field-specific contaminant migration information.

*Ravenglass site (England) – Testbed to examine cycling in redox stratified sediments.* The Ravenglass salt marsh is within the Sellafield site on the north west coast of England. Sellafield was originally established in 1947 to support the UK nuclear weapons program and effluents from this site are, by far, the largest source of Pu discharged in all of western Europe (276 kg Pu). The Ravenglass saltmarsh is a highly dynamic system located 10 km south of the Sellafield site and is a low energy, intertidal region that accumulates Sellafield-derived contamination. To determine the factors affecting the mobility of Pu in these redox stratified sediments, we conducted a series of desorption experiments under both oxic and anoxic conditions over a nine-month period. The results of this work suggest that Pu desorption (and mobilization) increases under anoxic conditions in estuary sediments. This is leading to a paradigm shift in our understanding of Pu redox chemistry and its impact on radionuclide migration.

*Hanford site (Washington, US) – Testbed to examine legacy waste impacted conditions.* The unlined Z-9 trench at the Hanford Reservation (200 Area) received large volumes (~4x10<sup>6</sup> liters) of Pu processing waste consisting of high salt (~ 5M NO<sub>3</sub>, ~ 0.6M Al), acidic (pH ~ 2.5) solutions, which also contained the organic solvents: CCl<sub>4</sub>, TBP, DBP, and lard oil. A small fraction of Pu migrated deep into the subsurface vadose zone to depths of 37 m. Binary batch experiments containing aqueous phase and organic phases demonstrated Pu was sequestered by the organic phase at pH 2 and 3 and partitioning decreased with increasing pH. Thus, Pu may be mobilized into the aqueous phase during infiltration of low ionic strength waters.

*Nevada National Security Site (Nevada, US) – Testbed to examine wet-dry cycling using ephemeral stream beds.* Ephemeral stream beds at Rainer Mesa, Nevada (site of nine underground nuclear tests) is used to evaluate the influence of stream bed wet-dry cycling on actinide migration. Continuous discharge from a perched aquifer drains into a series of unlined containment ponds located in an ephemeral stream bed. While radionuclide concentrations in the discharge remain below permissible limits, distribution of contaminants in the pond sediments and shallow groundwater underlying the ponds are unknown. In collaboration with Mission Support and Test Services, LLC, we conducted the first sampling trip to the E-Tunnel pond system in April 2021. Thirteen sediment cores (6” deep) were collected to examine actinide and trace metal distributions. Another sampling campaign is planned during wetter conditions to capture contaminant distribution in pond sediments and porewater in a fully saturated state.