**Argonne National Laboratory Wetland Hydrobiogeochemistry SFA**
**FY2019 Annual Progress Report**
**For the BER Subsurface Biogeochemical Research Program**
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### 1. Program overview

Wetlands are landscape features where standing water is present all or part of the time. Within wetlands, the movement of water and the biogeochemically catalyzed transformations of its constituents determine the mobility of nutrients and contaminants, the emission of greenhouse gasses into the atmosphere, carbon (C) cycling and sequestration in subsurface environments, and the quality of water itself. In terms of mass action as well as the extent of integration with other elemental cycles, biogeochemical processes within wetlands are largely driven by C biogeochemistry. Iron (Fe) and sulfur (S) are also abundant elements that are often found in wetlands. Their redox cycling is driven largely by microbial activity, and they are a significant component of major and minor elemental cycling and energy flux. In addition to greatly affecting elemental cycling and transport, wetlands provide many critical ecosystem services, such as water storage. While water <u>availability</u> is often a concern within arid regions of the western United States, higher population densities, continued residential and industrial development, and the importance of water in energy production also create strong concerns about water <u>quality</u> in the more humid parts of the eastern United States. In addition, extreme weather events and encroachment by humans can contribute to changes in water inputs and outputs, as well as the biogeochemical interactions within wetlands and the biota associated with them. Finally, although they are important, the explicit hydrologically driven wetland biogeochemical functions that control C, nutrient, and contaminant cycling and water quality are still not understood well enough to be adequately modeled. This is due in part to deficiencies in our current understanding of the complex and dynamic hydrologically driven biogeochemical processes that occur in wetlands.

The long-term, 10-yr objective of the Argonne *Wetland Hydrobiogeochemistry* Scientific Focus Area (SFA) is the *development of a mechanistic understanding and ability to model the coupled hydrological, geochemical, and biological processes controlling water quality in wetlands and the implications of these processes for watersheds commonly found in humid regions of the United States*. To accomplish this, the Argonne *Wetland Hydrobiogeochemistry* SFA will study wetland hydrobiogeochemistry with a focus on a riparian wetland field site at the Savannah River Site (SRS). The wetlands lie within Tims Branch at the SRS, whose waters ultimately flow into the Savannah River approximately 20 km downstream. This site is representative of many riparian wetlands found in the humid regions of the Southeast that have C-rich soils and high Fe content. However, it is unique in that it received large amounts of contaminant metals (Ni, Cr, Cu, Pb) and uranium (U) as a result of previous industrial-scale manufacturing of fuel and target assemblies at the M-Area Facility. Therefore, the function of the wetlands in relation to control of water quality, including the concentration of metals and U within the soluble and particulate components of groundwater and surface waters of Tims Branch, is a risk driver for DOE Environmental Management.

Members of the Argonne Wetland Hydrobiogeochemistry SFA, whose efforts are directly supported by the SFA or bring complementary expertise via synergistic collaboration, represent the critical components required to obtain our 10-yr objective. Members of the team from Argonne who are directly supported by the SFA include Kemner (PI, Biogeochemistry, Synchrotron Science), O'Loughlin (Co-PI, Biogeochemistry, Environmental Chemistry/Microbiology), and Weisenhorn (Wetland Ecology and Microbial Modeling). Members of the team from outside of Argonne who are directly supported by the SFA include Boyanov (Bulgarian Academy of Science, Physical Chemistry, Synchrotron Science), Kaplan (SRNL, Soil Science), Seaman (Savannah River Ecology Laboratory, University of Georgia, Study-site instrumentation and data collection), and Segre (Illinois Institute of Technology, Synchrotron Science, Assoc. Dir. of the Materials Research Collaborative Access Team/Environmental Collaborative Access Team [MRCAT/EnviroCAT] at the Advanced Photon Source [APS]). Members of the SFA who are not directly supported by SFA funds are supported through a variety of other means. Many have been

collaborating with the SFA for many years, have a proven record of productivity, and have alternative sources of support to synergistically work with the SFA team. Through other collaborative projects supported by other means, some institutions provide additional support to the project by supplying graduate students and postdocs, and by supporting visiting researcher sabbaticals at Argonne. Members of the team from specific institutions and their scientific expertise are Clemson (University class field trips to map U concentrations in the field, EPSCoR project): Powell (Actinide Chemist, geochemical and reactive transport modeling), and Martinez (Radiobiologist); Florida International University (DOE Environmental Management): Lawrence (Hydrological Modeling of Tims Branch watershed); Pacific Northwest National Laboratory (PNNL) (Environmental Molecular Science Laboratory [EMSL]): Hess (Environmental Chemistry, EMSL CESD Integrative Lead); Korea University: Kwon (Environmental Engineering, Biogeochemistry); China University of Geosciences (111 Project for Visiting Researchers, Groundwater Contamination and Remediation): Yan (Geochemistry), Wang (Biogeochemistry and President of the China University of Geosciences), Dong (Microbiology, Biogeochemistry), Deng (Wetland Biogeochemistry); Universidade Federal de Alfenas: Rodriguez (Environmental Engineering, Biochemistry, wastewater treatment and floc formation); Argonne National Laboratory (KBase): Henry (Metabolic Modeling, KBase PI at Argonne); Lawrence Berkeley National Laboratory (LBNL) (ENIGMA, KBase): Adams (Microbiology, ENIGMA Co-PI), Arkin (Microbiology, ENIGMA PI, KBase PI at LBNL), and Chakraborty (Microbiology, ENIGMA-supported researcher); University of Leeds: Mishra (Synchrotron characterization of C and S speciation).

The overarching hypothesis of our work is that *hydrologically driven biogeochemical processes that create redox dynamic conditions from the nanometer to meter scales are a major driver of groundwater and surface water quality within riparian wetland environments*. A focus on major (e.g., C and Fe) biogeochemical cycles and their controls on U hydrobiogeochemistry and water quality within the Tims Branch wetlands builds on decades of synchrotron-based biogeochemistry and omics-based microbial community research expertise previously developed within the Argonne Subsurface Biogeochemical Research (SBR) Program SFA. In addition, the focus on hydrobiogeochemistry within a riparian wetland in the Southeastern United States complements and expands the portfolio of existing SBR SFA field site testbeds concerned with mountainous watersheds (LBNL SFA), shallow alluvial groundwater systems (Stanford Linear Accelerator [SLAC] SFA), hydropower-impacted and highly managed rivers (PNNL SFA), and critical terrestrial-aquatic interfaces within streams (ORNL SFA) in both arid and humid regions of the United States that play major roles in controlling groundwater and surface water quality. As such, this Science Plan aligns with the SBR program within the Climate and Environmental Science (CESD) Division of the DOE Biological and Environmental Research (BER). In addition, because wetlands, by definition, encompass both terrestrial and aquatic environments, our investigation of the Tims Branch riparian wetlands and watershed complement burgeoning efforts within the Terrestrial Ecosystem Science Program of BER to better understand critical earth system terrestrial-aquatic interfaces.

We identified three major components (focus areas) of the Tims Branch riparian wetland that represent critical zones containing hydrologically driven biogeochemical drivers, which determine water quality: sediment, rhizosphere, and stream. These three focus areas are interdependent and must be considered as a whole for a systems-level understanding of our overarching hypothesis. Within these three focus areas, we identified two common thematic knowledge gaps that inhibit our ability to predict controls on water quality:

*(1)* *In-depth understanding of the molecular-scale biogeochemical processes that affect Fe, C, and contaminant speciation within the wetland sediment, rhizosphere, and stream environments; and*

*(2)* *In-depth understanding of hydrologically driven biogeochemical controls on the mass transfer of Fe, C, and contaminants within wetland sediment, rhizosphere, and stream environments.*

Holistically addressing 18 specific hypotheses related to these two knowledge gaps within the sediment, rhizosphere, and stream environments organizes the SFA in its development of a hydrobiogeochemical conceptual model of the Tims Branch riparian wetland.

From the beginning of this project, we strongly emphasize our integrated lab- and field-based experimental research and field monitoring. This enables us to derive key model parameters as we simultaneously develop the mechanistic understanding necessary for modeling approaches to predict wetland controls on water quality. Materials collected from sediment, rhizosphere, and stream environments will be analyzed to identify major hydrologically driven biogeochemical processes that affect surface and ground water within wetlands. Besides standard analysis approaches, we will use unique capabilities (synchrotron-based approaches at the APS at Argonne, omics-based approaches and collaborative research with KBase researchers at Argonne and LBNL, and mass spectrometry-based approaches to characterize C chemistry through collaboration with scientists at the EMSL at PNNL) to analyze field and lab materials.

Via collaborations with university-led projects that are supported by the SBR program, the modeling approaches we will integrate with our work in the early years of this project are limited primarily to reactive transport models (RTMs) of lab-based mixed batch reactors, diffusive and advective flow experiments, and small-scale field observations. We will supplement RTMs with metabolic modeling of organisms and interacting consortia to more accurately capture the role of microbial communities in mediating biogeochemical transformations. These models will be used for hypothesis testing, and to analyze the sensitivity of hydrobiogeochemical processes in determining water quality. In addition, the iterations between lab- and field-based experiments in concert with modeling will improve both aspects of the work. In later years of the SFA, we envision a stronger emphasis on field-scale observations and characterizations and their coupling with hydrological system model development of the Tims Branch riparian watershed to explain the particulate and soluble fractions of nutrient and contaminant element transport via surface water and groundwater flow.

A preliminary hydrological model has already been developed for the Tims Branch. It is critical for ultimately modeling coupled hydrological and biogeochemical controls, and it provides key insights and data related to surface water and groundwater flow within the watershed. These are critical for identifying hydrological drivers of the biogeochemical processes to be studied and to be integrated into RTMs. Finally, in the next decade, the hydrological model of Tims Branch (~6 km in length) we will develop—with reactive transport models embedded within it—will enable us to explore the effect of these integrated models on the National Water Model, which makes use of 1-km grids.

## 2.  Scientific Questions

As discussed in the previous sections, the hydrologically driven and coupled biogeochemical cycles of Fe and C within redox dynamic wetland environments can exert strong control over the transformation and transport of major and minor elements including U and contaminant metals within surface water and groundwater in Tims Branch. While the molecular scale chemical states and transformations of Fe and C can greatly affect their solubility, they also can greatly affect the solubility of U and contaminants within surface water and groundwater. Thus, the ability to understand and predict the behavior of major and minor elements in natural systems, including nutrients and contaminants, is predicated on identifying molecular-scale qualities of an element that determine its partitioning between solid and solution phases. The transport of major elements and contaminants in subsurface environments is also influenced by advection, dispersion, and diffusion processes, as well as their association with suspended solids and complexing molecules within surface and groundwater. Thus, the molecular-scale chemical reactions occurring along the flow path—coupled with reactions and transport that are greatly affected by water—determine the spatial and temporal distribution of the elements. Therefore, we identified two major knowledge gaps that hinder our ability to understand and predict the role of riparian

wetlands in determining the quality of water associated with them. The knowledge gaps (KGs) are as follows:

(1) *In-depth understanding of the <u>molecular-scale biogeochemical processes</u> that affect Fe, C, and contaminant speciation within the wetland sediment, rhizosphere, and stream environments; and*

(2) *In-depth understanding of hydrologically driven biogeochemical controls on the <u>mass transfer</u> of Fe, C, and contaminants within wetland sediment, rhizosphere, and stream environments.*

To summarize the importance of these Knowledge Gaps, *a fundamental knowledge of the specific molecular-scale biogeochemical processes and their controls on the mass transfer of Fe, C, and contaminants is needed to attain our ten-year goal to develop a mechanistic understanding and ability to model the coupled hydrological, geochemical, and biological processes controlling water quality in wetlands and the implications of these processes for watersheds commonly found in humid regions of the United States.*

We are leveraging decades of total experience in synchrotron-based Molecular Environmental Science (MES) research among members of the Argonne SFA team, the unique capabilities of the APS, and our unique local association with the APS to pursue the development and advancement of a number of synchrotron-based capabilities at the APS, particularly capabilities focused on x-ray absorption spectroscopy (XAS) and x-ray microscopy, that are critical to the Argonne SFA and are of service to the SBR scientific community. In addition, we are leveraging unique capabilities at Argonne that enable the use of DNA sequencing technologies and bioinformatics approaches being developed within the KBase project to determine microbial community structure and function in our samples. The further development and integrated use of synchrotron-based and bioinformatics approaches with field and standard laboratory-based biogeochemical experimental approaches for characterizing microbiological and geochemical processes controlling transformations of major/minor elements and contaminants in the subsurface is central to the Argonne Wetland Hydrobiogeochemistry SFA and represents unique capabilities that Argonne contributes to the SBR mission.

Seventeen hypotheses related to these knowledge gaps, organized under the three focus areas (sediment, stream, and rhizosphere), guide the experimental design of the Argonne Wetland Hydrobiogeochemistry SFA so as to investigate nanometer-scale transformations and meter-scale transport. Experiments are done using mixed batch reactors (MBRs) and columns in combination with field site observations and characterizations.

### 3. Argonne Wetland Hydrobiogeochemistry SFA Program Structure

The integration of scientific expertise with the unique technical capabilities available at the APS at Argonne, the approaches being developed within ENIGMA and KBase, and the capabilities being leveraged at the EMSL are all critical to developing the predictive understanding of the role wetlands play in determining water quality. Our management plan is organized to ensure efficient integration of (1) technical capabilities, (2) field- and lab-based methods in hydrobiogeochemistry and microbial ecology, and (3) modeling approaches through either Argonne capabilities or collaborative arrangements with other national laboratories or universities. This plan will enable us to achieve our long-term objective to *develop a mechanistic understanding and ability to model the coupled hydrological, geochemical, and biological processes controlling water quality in wetlands with implications for watersheds commonly found in humid regions of the United States.* The management plan is designed to (1) facilitate communication between the DOE-BER CESD-SBR program office, Argonne managers, and SFA investigators and (2) coordinate collaborations among Argonne and external researchers to support our scientific objectives.

The Argonne Wetland Hydrobiogeochemistry SFA research efforts reside in the Biosciences Division, an organizational unit within the Computing, Environment, and Life Science (CELS) Directorate (see figure) at Argonne. Presently, the Deputy Associate Laboratory Director (ALD) for

CELS serves as the research manager for the SFA; the PI and Co-PI are direct reports in matters related to the SFA. The CELS Deputy ALD, the PI, and Argonne Biosciences Division Director work collaboratively in matters related to the integration and development of new Biosciences Division capabilities that might benefit the SFA, with the PI reporting directly to the Argonne Biosciences Division Director. The Associate Director of MRCAT/EnviroCAT works collaboratively with the PI to optimize beamline developments and beamtime allocations to enable highly productive synchrotron-based work on this
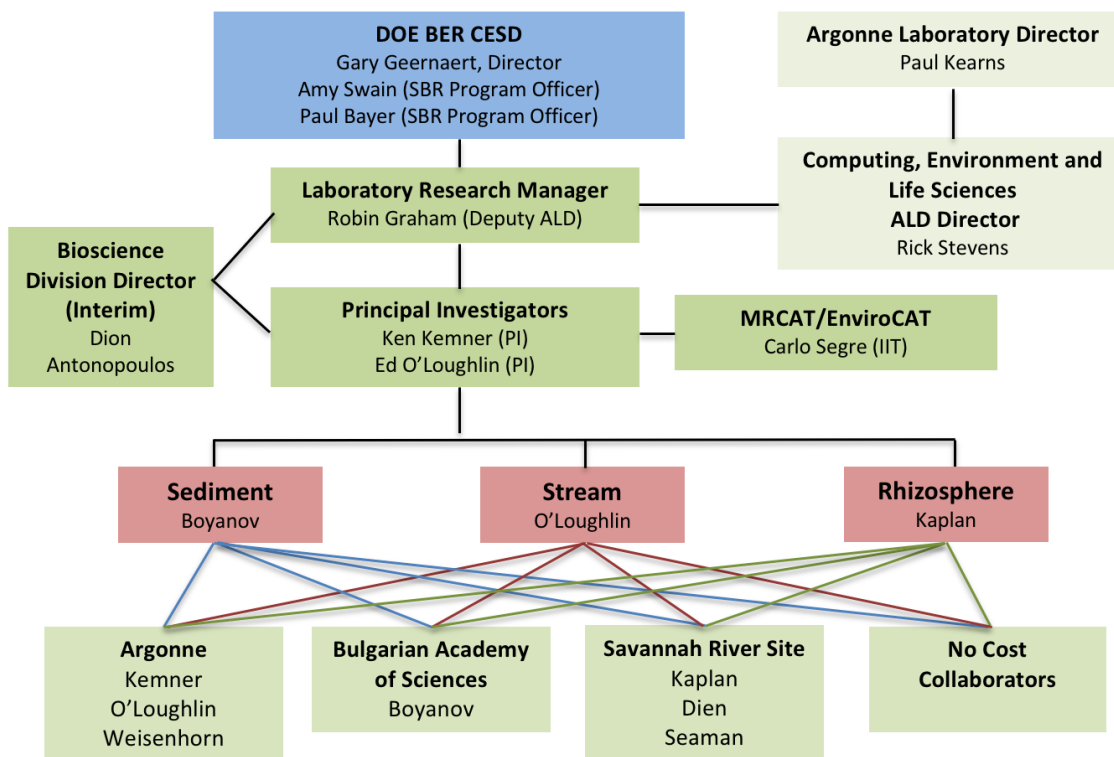


Management organization chart for the Argonne Wetland Hydrobiogeochemistry SFA (The lines indicate communication among the parties.)

project. The leads of the three focus areas work closely with the PI and all SFA members to integrate and synthesize results from each focus area into a systems approach to understand the Tims Branch wetland. The management plan currently includes the subject area leadership expertise of key investigators, internal and external to Argonne, in the following six broad subject areas that are essential to the Argonne SFA Science Plan: (1) biogeochemistry (Deng, Dong, Kaplan, Kemner, Kwon, Mishra, O'Loughlin, Rodriguez, Seaman, Wang, Weisenhorn, Yan); (2) omics-enabled science including development and integration of KBase tools and capabilities associated with the ENIGMA project (Adams, Arkin, Chakraborty, Henry, Weisenhorn); (3) characterization of C, Fe, S, and contaminant speciation (Boyanov, Hess, Kemner, Mishra, O'Loughlin, Pasa-Tolic); (4) synchrotron beamline development and applications (Boyanov, Kemner, Segre); (5) field-based observations and manipulations in Tims Branch watershed (Dien, Kaplan, Martinez, Powell, Seaman); and (6) hydrological and systems-based modelling (Kaplan, Lawrence, Powell, Weisenhorn). This scheme stabilizes the SFA by providing redundancy in each subject area while also offering flexibility to add or change subject area expertise as needed to achieve the program objectives.

The research manager, with support from the PI, is responsible for communicating with program managers in the SBR office regarding program direction and progress. The research manager is responsible for transmitting information between the SBR program office, the CELS ALD and the Laboratory Director, and the SFA PI and Co-PI. The research manager, in collaboration with the PI, is also responsible for ensuring that Argonne capabilities and expertise are integrated into the SFA research in a way that advances that research for the benefit of the SBR program. As new capabilities become available at Argonne, the research manager, in collaboration with the PI, is responsible for assessing their applicability to the existing SFA work and their possible integration into new research avenues. The research manager and PI work together to determine the need for new hires and discuss funding allocations for tasks in the SFA; the research manager has final approval authority for all hires and major funding decisions.

The PI is responsible for communicating with the SFA team members to integrate the experimental work efficiently. This communication occurs through regular group meetings (at least monthly and often weekly) at which the PI, Co-PI, and local members of the SFA discuss research progress in the context of the stated research objectives and deliverables. The PI is responsible for providing reports on program progress to the research manager each quarter and assists the research manager with presentations to the SBR program managers, as well as to the CELS ALD.

Focus area leads, in collaboration with the PI and Co-PI, are responsible for outlining the scope of work in respective focus areas, to ensure the timely completion of tasks and generation of deliverables. This responsibility includes ensuring that the work is done by the appropriate staff at Argonne, in coordination with subcontractor institutions and "no-pay" collaborators, and that the research manager and PI are aware when new hires are needed. The focus area leads coordinate regular conference calls between Argonne and subcontractor team members to communicate research progress; annual visits to Argonne or the Savannah River Site by collaborators for an "all-hands meeting" is encouraged.

The key investigators in the three focus areas (sediment, rhizosphere, and stream) ensure the availability of interdisciplinary expertise required for the successful completion of our scientific objectives. Key investigators are expected to (1) facilitate communication of experimental results and a team approach to the analysis and interpretation of those results; (2) seek new research opportunities, based on their areas of expertise, that complement the current SFA goals; and (3) provide guidance to the research manager, PI, Co-PI, and focus area leads regarding future research directions. Key investigators are also expected to attend one or more scientific conferences each year to present results from their key areas of experimentation; they will also assist with, and sometimes lead, the preparation of reports, manuscripts, and presentations.

*The key Argonne scientific staff responsibilities and level of support from SFA for FY2019 are detailed below.*
Dr. Ken Kemner's efforts (50%) has him serving as the PI for the SFA and working closely with the focus area (sediment, rhizosphere, and stream) leads and all other researchers to ensure a systems approach to the work.
Dr. Ed O'Loughlin's efforts (65%) has him serving as the Co-PI for the SFA and lead for the stream focus area.
Dr. Pamela Weisenhorn is an early career scientist and her efforts (25%) have her working closely with the focus area leads to integrate KBase and microbial community model development into the research.

*Key non-Argonne SFA members who are supported by SFA funds are described below.*
Dr. Dan Kaplan (SRNL) is the rhizosphere focus area lead and is in charge of leading Tims Branch study site instrumentation and data collection, and sample collection. Dr. Kaplan participates in SFA coordination conference calls (at least monthly), attends the ESS annual PI meeting, and attends SFA All

Hands Meetings (in person). Dr. Kaplan coordinates the efforts of Dr. John Seaman and Dien Li at the Savannah River Ecology Laboratory that are related to SFA work within Tims Branch at SRNL. Dr. Kaplan also works closely with Dr. Seaman to coordinate the use of Dr. Seaman's biogeochemistry labs during SFA member field campaigns within Tims Branch.

Dr. Boyanov (Bulgarian Academy of Science) is the sediment focus area lead and co-lead for synchrotron x-ray spectroscopic characterization of field and lab-generated materials. Dr. Boyanov travels from Bulgaria to Argonne so that he may participate in experimental beam runs at the APS. He remains at Argonne for approximately an additional week after each of the six beam runs per year to participate in face-to-face collaborative discussions with other members of the Argonne SBR SFA team. He also participates in weekly group meetings via Skype, the yearly ESS PI meeting (in person), and SFA All Hands Meetings (in person).

Finally, a few changes to the Management Organization chart presented above are worthy of being noted. Specifically, Dr. Dion Antonopoulos replaced Dr. Philippe Noirot on June 10, 2019 as Director of the Argonne Bioscience Division. Presently, Dr. Antonopoulos is listed as the interim Bioscience Division Director. Dr. Antonopoulos was a member of the Argonne SBR SFA during FY13-FY18 and continues to have a good collaborative working relationship with members of the Argonne SFA. In addition, Dr. Robin Graham has announced her intention to retire before the end of FY19. Should her position of Deputy Associate Laboratory Director not be filled, we envision Dr. Christina Negri (Argonne Environmental Science Division Director) taking on some of the responsibilities that were described above in this section. Members of the SFA will work closely with both the Bioscience Interim Division Director (Dr. Antonopoulos) and the Environmental Science Division Director (Dr. Negri) to maintain communication between DOE BER and the Argonne SFA and to advance the SFA.

## 4. Performance milestones and metrics
### a. FY 2019 Scientific progress
#### i. Progress toward milestones

The milestones proposed for FY2019 are listed below followed by a brief description of our progress to date. We will have met 15 of 19 of our milestones for FY 2019. Two of the four milestones that were not met were delayed as a result of delayed funding appropriations to SRNL. In addition, we are ahead of schedule in meeting milestones originally scheduled for FY2020. The four milestones not met in FY2019 are planned for the first half of FY2020 or sooner. At the end of this section we also provide descriptions of synergistic activities between the SFA and KBase, ESS-DIVE, and IDEAS-Watersheds.

**Year 1**

- **Install ISCO stream samplers, diffusion porewater samplers, potentiometric head wells at the Tims Branch study site to collect samples for laboratory studies and to be used to provide basic characterization data (background information relevant to several hypotheses).**
  Some delay in field work occurred due to a delay in establishing the contract with SRNL. Scientists from Florida International University, Georgia Tech, University of Minnesota, University of Georgia, Clemson University, and Analytical Instrument Systems, Inc. (SBIR program) collected samples or conducted experiments at the field site. Staging of sampling equipment, laboratory measurements, sample preparation/preservation, and shipping were conducted at the Savannah River Ecology Laboratory, University of Georgia (Seaman). Some of the results from these external studies are described below. Additionally, several extensive field sampling campaigns were conducted that provided samples which were used by the ANL-SFA team. An ISCO sampler has been installed immediately below the Steed Pond dam but continues to have solar-energy electrical problems. Some new parts have been ordered and will be installed in July. A second ISCO sampler has been identified and will be deployed downstream next winter. Contracts have been set up to fabricate two types of porewater diffusion samplers: one

contract with Clemson and the other with SRNL. These will be deployed in August. Nine potentiometric head wells were installed in January. Additional wells will be deployed this fiscal year as we learn more about the site hydrology.

- **Determine U distribution at the meter scale in Tims Branch wetland to be used to provide an estimate of the source term (background information relevant to several hypotheses).**
  In collaboration with work sponsored by NNSA, helicopter fly-over gamma analyses were conducted in September 2018. The flight plan involved flying at 72 kph at ~30 m above tree height and along parallel flight paths that were 25 m apart. These results provided us with a map of the U hot areas by detecting $^{234m}$Pa and will be used to develop an inventory of the U in Tims Branch. The spatial resolution over the 350-ha contaminated area was 25 meters. Also, in collaboration with NNSA, five backpacks with NaI gamma counters, GPS units, and computer tablets were used to collect data that could be used to make a U concentration map, but at much greater resolution of 3 m. In collaboration with SRNL (Dr. Dan Kaplan), Clemson University (Dr. Powell and Dr. Martinez) and University of Georgia (Dr. Seaman), the walkover mapping was conducted over the course of a week. Each day included instructions and planned lessons on the technology and at the end of each day, participants worked on spectra analysis and compilation of the data into maps. 149,000 spectra were collected and ¾ of the contaminated site was mapped. The remaining mapping will be completed in December 2019. The walkover data was consistent with the flyover data, but because of much lower detection limits, the former determined that the contaminated area was in fact about 5 times greater, albeit the estimated U inventory only went up slightly, about 4%.

- **Conduct an initial survey to determine the extent and the distribution of oxidized rhizospheres (red clay) in reducing bulk soils (gray gleied soil) (Rh KG1.1).**
  Very little progress was made on this milestone because Kaplan has been focusing more on instrumenting the field site. Analyses of moss plants indicated elevated U concentrations with respect to other plants. Furthermore, elemental mapping at MRCAT showed high concentrations of U (and other contaminants including Ni and Zn) were detected along the central vein of the moss. While rhizosphere XAS measurements were made, the results have not been fully analyzed.

- **Collect rhizosphere and bulk soil samples from contaminated portions of Tims Branch and determine U distribution; prepare manuscript (Rh KG1.1)**
  This task has not been initiated. It has been rescheduled for December 2019.

- **Collect plant roots (and root plaques) from contaminated portions of Tims Branch and determine U distribution with respect to P and Fe; prepare manuscript (Rh KG1.2 and Rh KG1.3)**
  This task has not been initiated. It has been rescheduled for Feb 2020.

- **Initiate surveys of U concentrations in the sediment at various locations of the Tims Branch field site (Sd KG 1.1)**
  Although gamma radiation mapping provided U concentration mapping information on the X-Y coordinates, the depth of U contamination at the site remains unknown. To provide greater understanding of the depth distribution, Clemson University will be conducting depth-discrete U measurements from 12 1-m cores strategically collected from various classes of soil types and strategically located in relation to Tims Branch. These samples have been collected and analyses and photo archiving has been initiated. Initial results show that the maximum concentration exists at a depth of 12 cm, with elevated concentrations above this maximum and U concentrations returning to background levels at depths >17 cm depth. Hot particles with 10% U were identified using SEM/EDX.

As described in more detail above, flyover and walkover measurements of specific radiation markers were conducted over a large area to estimate the contaminant inventories at the site. The same data were used to identify sediments in the field with high concentrations of U so they can be targeted for microbiological and geochemical analyses. A zone with elevated U concentrations was identified from the aerial gamma maps with 25 m resolution, and several paths within it were surveyed with the backpack gamma detectors. We currently have a 1 km path mapped at 3 m resolution which was used to select sediment sampling sites. The developed approach will continue to be used in the future for identifying new areas of interest for sampling aimed at relating biogeochemical processes to U accumulation in the field.

- **Collect sediment cores based on the results of U concentrations in the field (Sd KG 1.1-1.4)**
  The surveys of U accumulation in the field informed the selection of locations where we have collected so far 15 sediment cores in 5 sampling campaigns (0-30 cm depth, 3 cm diameter). The cores were preserved anoxically and sent to Argonne for microbiological and geochemical analysis. The core locations varied from waterlogged sediments near a stream to the drier areas farther away and higher up from the water surface, some with vegetation and apparent higher organic matter content, and some without. The common parameter in the sampling was locations with high U concentration, between 30 and 600 ppm. The sampling design was aimed at examining the speciation of U at locations with different biogeochemical conditions in the field in order to look for a connection between the two, as well as understanding the variability of U species in the field from the perspective of contaminant migration.

- **Characterize samples from the cores using synchrotron techniques to determine U valence state and distribution with depth and with core location (Sd KG 1.1)**
  The collected cores were sectioned under anoxic conditions at Argonne and samples from different depths and locations were prepared for U $L_{III}$-edge x-ray spectroscopy analysis at the Advanced Photon Source. The results of these measurements revealed that the valence state of U varied between U(IV) and U(VI), depending on whether the sediments were near the stream and saturated vs sediments that were dry. The sediments near the surface showed U(VI) regardless of water saturation, whereas organic-rich saturated sediments at intermediate depths (7-15 cm) showed U(IV). An interesting observation was that the U(IV) at all sampled locations was not the low solubility mineral uraninite ($UO_2$) predicted by thermodynamic calculations. This suggests the need for further studies on the factors controlling the speciation of U(IV). The variability in U valence and speciation in the field suggests a complex behavior of this contaminant, implying significant uncertainty in the prediction of its mobility and requiring further studies.

- **Perform microbial characterization of the site, with emphasis on sediment, rhizosphere, and stream compartments**
  Preliminary analysis of microbial communities from sediment, rhizosphere, and stream (floc) samples have revealed an unexpectedly great diversity in floc communities as compared to sediment (mineral, organic, and rhizosphere component) samples. Dominant microbial taxa in the iron oxide flocs included members of phylogenetic groups involved in many elemental cycles, including iron (*Sideroxydans*), sulfur (*Desulfuromonas* and *Thiovirga)*, and reduced carbon (*Methylococcaceae)*. This is consistent with floc formation resulting from groundwater-surface water mixing. Meanwhile, all sediment components were dominated primarily by taxa in the *Acidobacteria*, with the three most dominant, three of five most dominant, and four of five most dominant taxa from this clade in organic sediment, mineral sediment, and rhizosphere, respectively. *Nitrospira* taxa, commonly chemolithoautotrophs which are responsible for removal of nitrate contamination of drinking water, were dominant taxa in both organic sediment and rhizosphere. Recently, some members of this genus have been identified as Comammox, bacteria capable of performing both steps of nitrification.

Over a hundred samples have been collected for a Tims Branch-wide study of microbial community composition and structure. This study was designed to capture shifts in microbial communities as a result of heterogeneity in soil moisture, redox, micro- and meso-topography, soil type, slope/relief, vegetation type, and contamination status (concentration and identity of contaminant). An additional 30+ samples were collected to examine the effects of stannous chloride treatment of groundwater mercury contamination on stream (aqueous) and streambed sediment microbial communities.

- **Characterize elemental and organic matter content and relate to the observed U valence state and speciation (Sd KG 1.1-1.2)**
  Sediments were digested in acid to dissolve the metals and contaminants from the sectioned cores and the extracts were characterized by ICP-OES for elemental content. This has been done for about 20-30% of the cores collected so far, the remaining core samples are awaiting analysis following instrument repair. Once the analysis of the cores is completed the observed elemental content will be correlated with observed U speciation. The characterization of the organic matter in the sediments is pending, a limited number of samples have been measured by FTICR-MS at EMSL and the analysis of those data is ongoing.

- **Initiate laboratory experiments with defined mineral-microbe-organic matter assemblages: study the effect of ligand:U ratio on U speciation and build a database of U EXAFS spectra that enables the analysis of U speciation in the sediment (Sd KG 1.1-1.2)**
  The observation of uncharacterized, non-uraninite U(IV) species in the saturated sediments prompted further studies on the factors controlling the speciation of U(IV). Building on prior SFA work, we began investigations on the effect of added organic matter (Suwanee River Humic Acid, HA) on the speciation of U(IV) adsorbed on the surface of rutile (titanium dioxide). Two U:mineral ratios were investigated so far with synchrotron spectroscopy, 250 μM U added to 5 g/L and 30 g/L $TiO_2$. Under the 5 g/L $TiO_2$ conditions, U(IV) was observed to be in the form of uraninite, independent of the concentration of HA (0-400 mg/L). Under the 30 g/L $TiO_2$ conditions, U(IV) was observed to be in the form of adsorbed U(IV), with little effect of the HA (0-400 mg/L) on the spectrum. These results suggests a relatively minor role of the HA on U(IV) speciation under the studied conditions. Further studies under lower U:mineral ratios and higher HA concentrations that may be relevant to natural environments are planned to understand the role of organic matter in the speciation of U(IV) observed in the sediments.

- **Develop and test procedures (e.g., filtration, flow field-flow fractionation, etc.) to separate different colloidal fractions from the sediment; determine U and other elemental concentrations in the different size fractions (Sd KG 1.3)**
  This task has not been initiated. It has been rescheduled for October 2019.

- **Characterize samples from the sediment cores using spectroscopy and wet chemical techniques to determine Fe valence state with depth and with core location (Sd KG 1.4)**
  The sediment cores obtained from the field site were sectioned under anoxic conditions at Argonne and samples from different depths were analyzed using Fe K-edge x-ray spectroscopy at the Advanced Photon Source. About half of the collected cores were analyzed. The results reveal that the average valence state of Fe in the sediments is consistently more reduced in waterlogged locations at intermediate depths, which indicates overall reducing conditions in these areas and correlates with the observed reduced valence state of U. Although more oxidized than waterlogged locations, drier locations or locations near the soil surface still showed the presence of significant Fe(II). These areas however showed U(VI) in the U XANES analysis, which indicates that a certain amount of Fe(II) in the sediment is not available for reduction of U(VI). Further work in controlled reactors is planned to understand the reasons for this limitation in

sediment redox capacity. The spectroscopy results also correlate well with wet chemistry measurements of Fe(II) and total Fe in the solids. Further work correlating U and Fe valence state in the sediments is planned for Years 2 and 3.

- **Initiate routine observation and monitoring of stream flow, water chemistry, suspended solids (including incidents of floc formation), water table, near-stream sediment porewater, and meteorological data—with more aggressive sampling surrounding storm events (background information relevant to several hypotheses, particularly St KG 2.1, and St KG 2.2)**
  In collaboration with the University of Minnesota (Drs. Santelli and Ng), surface water gauges and groundwater piezometers have been installed in the control area in the stream channel in sections without floc (losing stream) and with floc (gaining stream) as well as a floc dominated riparian wetland adjacent to the stream. Rhizon samples and peepers were used to collect porewaters for measurement of dissolved oxygen, nitrate, sulfate, sulfide, metals, methane, and organic acids. As mentioned previously, an ISCO sampler has been installed immediately below the Steed Pond dam but continues to have solar-energy electrical problems. Some new parts have been ordered and will be installed in July. A second ISCO sampler has been identified and will be deployed downstream next winter. Contracts have been set up to fabricate two types of porewater diffusion samplers: one contract with Clemson and the other with SRNL. These will be deployed in August.

- **Collect Fe flocs for characterization of native microbial communities, elemental composition, Fe and U speciation, and carbon characterization (background information relevant to St KG 1.1, St KG 1.2, and St KG 2.3)**
  Abundant reddish-brown flocs are routinely observed along Tims Branch and floc material has been collected on several occasions from multiple locations. The flocs contain high levels of Fe (9.7%), P (2.7%), S (1.2%), and Al (0.4%), and other less abundant elements. The Fe in the flocs consists primarily of ferrihydrite (83%) and lepidocrocite (17%) as determined by Fe K-edge EXAFS spectroscopy. The U content of the flocs varies considerably. U concentrations in flocs upstream of the M-Area discharge were below our detection limit (< 50 ppb), while flocs within and downstream of the former Steed Pond area contained 150–600 ppm U. The amount of U in the flocs was 5.5 times greater than the highest concentration of acid-extractable U in streambank sediments collected at the same time as the floc material. The U $L_{III}$-edge EXAFS data from the flocs are similar to data from a U(VI) precipitate retained on 0.22 μm filter from a reactor with 250 μM $U^{VI}$, 20 mM MOPS pH 7.2, 20 mM NaCl electrolyte, and 2mM $NaHCO_3$ as a complexant. The identity of the precipitate is currently being determined, however, the EXAFS data appear most similar to published data for compreignacite, $K_2$- or $Na_2$-$(UO_2)_6O_4(OH)_6 \cdot 8(H_2O)$. The microbial communities in the flocs are surprisingly diverse with highly abundant members of the floc including: *Sideroxydans* (iron oxidizers), *Methylococcaceae* (methanotroph - multiple high abundant OTUs), *Desulfuromonadales* (iron and sulfur reducers), *Thiovirga* (sulfur oxidizers), and a whole host of "*Betaproteobacteria*" OTUs.

- **Begin batch reactor experiments investigating the potential role of IOB in the formation of Fe flocs in Tims Branch (St KG 1.1)**
  This task has not been initiated. It is scheduled for September 2019.

- **Initiate batch reactor experiments investigating the extent to which Fe flocs sequester and stabilize U (St KG 1.2)**
  This work is scheduled to begin in August 2019.

- **Begin batch reactor experiments to examine the stability of U sequestered in Fe flocs under anoxic conditions (St KG 1.3)**

Tims Branch water and floc material were combined to construct microcosms to examine the effects of anoxia on the redox state and speciation of floc-associated U. The microcosms were prepared in serum bottles containing 50 mL of floc suspension and 100 mL of headspace. Treatments consisted of oxic ($\sim$21% $O_2$ headspace) and anoxic (Ar headspace) conditions. Three anoxic systems were prepared; unamended, acetate amended, and $H_2$-amended. Flocs collected and maintained in microcosms under oxic conditions were stable for > 10 d, exhibiting substantial aerobic respiration and no apparent reduction of Fe(III). Over the same time, flocs exposed to anoxic conditions showed significant production of Fe(II) and carbon dioxide. Higher levels of Fe(II) and carbon dioxide were observed in the acetate and hydrogen amended anoxic microcosms. The hydrogen and acetate microcosms became methanogenic within 4 d. U $L_{III}$-edge XANES spectra of the flocs indicates that U in the oxic microcosms remains as U(VI) at the end of the 11 d incubation and U EXAFS indicates no change in its chemical speciation (i.e., U remains in the form of a putative U oxyhydroxide similar to compreignacite, $K_2$- or $Na_2$-$(UO_2)_6O_4(OH)_6 \bullet 8(H_2O)$). In the unamended anoxic microcosm, 50% of the U was reduced to U(IV) within 11 d, while in the hydrogen- and acetate-amended anoxic microcosms, all of the U was reduced to U(IV). U EXAFS data from the hydrogen and acetate amended anoxic microcosms indicate mononuclear U(IV) species that do not have the peak indicative of the U-U coordination in uraninite. The identity of this U(IV) species is currently being defined, the data suggest that U(IV) in the floc material is not coordinated to phosphate groups.

- **Begin laboratory experiments examining the stability of colloidal U under controlled conditions representative of conditions in Tims Branch (St KG 2.1)**
  This work is scheduled to begin in November 2019.

- **Systems Biology Knowledgebase (KBase) Synergies**
  In collaboration with developers on the KBase project (T. Gu, Q. Zhang), we have developed and beta-released the initial steps of an amplicon pipeline. This pipeline allows users to examine 16S, or targeted gene, abundance data in KBase for the first time and enables analysis of environmental and biogeochemical drivers of microbial community structure and function. In addition to pipeline design/conceptualization and expertise in analysis, our SFA contributed the initial datasets, which are publicly available through our KBase organization. Specifically, development included creation and release of the following:

  - Import Attribute Mapping as a new attribute mapping data type to link environmental data to amplicon (or other sequencing data matrix) based on sample ID or taxonomy. Developed within generics framework. (Released)
  - Update Attribute Mapping allows addition of environmental or other metadata to attribute mapping after it has been uploaded. (Beta)
  - Import Amplicon Matrix as two new data types: amplicon matrix to store abundance data (derived from sequencing data) and amplicon sets to store consensus sequencing reads. (Beta)
  - Compute Correlation Matrix creates a new data type consisting of two matrices: one stores strength of pairwise correlations and the other stores associated p-values. Developed within the generics framework and can be used on matrices other than amplicon matrix type. (Beta)
  - Compute Correlation Matrix Between Two Matrices calculates pairwise correlations between all elements of two matrices. Allows comparison of relationships between environmental factors and amplicons. Developed within generics framework and can be used on matrices other matrix types. (Beta)
  - Build Correlation Network generates a new data type and visualization of a filtered correlation matrix to show pairwise correlations. Developed within the generics framework, but requires correlation matrix. (Beta)

- **ESS-DIVE Synergies**
  We actively participated in community discussions with ESS-DIVE on sample identifiers, including the importance of ensuring clear, consistent, traceable linkages as samples are transferred between DOE user facilities including: KBase, JGI, EMSL, and ESS-DIVE. Our microbial characterization sampling effort was used as a ground test of the sample tracking protocol developed by ESS-DIVE for soil sampling.

  Data from our microbial characterization effort will be used as a test case for the transfer of both microbial (amplicon) and environmental data from ESS-DIVE to KBase. Additionally, we will work in collaboration with ESS-DIVE to establish data standards for key data products created using the amplicon pipeline we are co-developing in KBase to ensure provenance and generation of FAIR data products that can be easily transferred between the platforms. This includes the automatic creation of appropriate file level metadata for ESS-DIVE when downloading or transferring files from KBase.

- **IDEAS-Watersheds Synergies**
  A roadmap has been developed among the IDEAS-Watersheds team, PNNL (Hyun Seob-Song), and our SFA for the integration of output from metabolic modeling pipelines in KBase and the reactive transport models supported by IDEAS-Watersheds. This plan involves the generation of a KBase datatype whose output structure allows easy incorporation of reactions from metabolic models through the Alquimia interface. Forward progress is expected once KBase pipeline development results in the generation of final datatypes.

*ii. Science Highlights*

Argonne SFA team members have given at least 52 presentations, including 25 invited talks and 27 contributed talks (see Appendix B). Contributed presentations included five international conferences or universities (*Goldschmidt 2018*; *International Conference for X-ray and Optical Microscopy*; *International Conference on the Biogeochemistry of Trace Elements*; *International XAFS 2018*; China University of Geosciences-Wuhan University Colloquia). In addition to national scientific conferences, SFA scientific staff also presented invited talks at various universities and national laboratories, as well as invited talks for local community outreach opportunities.

Since our last SFA review (June 2018), 5 papers related to the SFA research efforts were accepted for publication (see Appendix A). Two additional manuscripts are presently in review. Specific Argonne SFA scientific highlights summarized from these five publications are given below to illustrate some of the foci of the SFA. The names of authors who are members of the Argonne SBR SFA are listed in bold letters.

M. E. Bishop, H. Dong, P. Glasser, B. R. Briggs, M. Pentrak, J. W. Stucki, **M. Boyanov**, **K. M. Kemner**, L. Kovarik, "Reactivity of redox cycled Fe-bearing sediments towards hexavalent chromium reduction", *Geochimica et Cosmochimica Acta* 252 (2019) 88–106
Structural Fe(II) in clay minerals and natural sediments is known to reduce Cr(VI) to Cr(III), but the effect of redox-cycled Fe-bearing natural sediments on Cr(VI) reduction kinetics is poorly understood. The objective of this study was to understand the kinetics and mechanisms of Cr(VI) reduction by Fe(II) in redox cycled natural sediment. Fe-bearing sediment was collected from the Ringold formation in the 300 area of Hanford, Washington, United States. Fe redox cycling of the sediment was accomplished via four cycles of bioreduction of structural Fe(III) in Hanford sediment and air oxidation of the resulting Fe(II). Bio-produced Fe(II) in Hanford sediment from each redox cycle was utilized to reduce Cr(VI) at three temperatures (10, 20 and 30 °C). The initial rate of Cr(VI) reduction generally increased with each redox cycle, which was more pronounced at high temperatures. The amount of Fe(II) oxidized to the amount of Cr(VI) reduced was close to the expected stoichiometric ratio of 3. Aqueous concentrations of Si, Al, and Fe revealed some dissolution of the sediment after reaction with Cr(VI). X-ray diffraction

(XRD) and scanning electron microscopy (SEM) detected secondary mineral formation. Mössbauer data showed that the oxidation of Fe(II) was coupled with the reduction of Cr(VI) but no Fe-oxides/oxyhydroxides formed. Transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), XANES, and EXAFS were performed for representative reduced Cr solids that formed from reduction of Cr(VI) by sediment-associated Fe(II) at 30 °C. TEM revealed that the d-spacing of Cr-reacted montmorillonite, a dominant Fe-bearing mineral in Hanford sediment, expanded from 10 Å to 13 Å. This layer expansion was likely due to intercalation of reduced Cr(III) into the interlayer space of the montmorillonite structure. EELS exhibited an L2 absorption peak at 586.0 eV and an L3 absorption peak at 577.0 eV, suggestive of Cr(III) in a hydroxide mineral phase. Similarly, XANES and EXAFS analyses confirmed Cr(VI) reduction to $Cr(OH)_3$ and indicated an edge-sharing coordination of the Cr(III) octahedra to 2-3 other Cr or metal ions. This study has important implications for understanding the reactivity of clay-rich sediment towards Cr(VI) reduction at contaminated sites and the stability of the reduced Cr(III).

K.A. Marquart, B.R. Haller, J.M. Paper, **T.M. Flynn**, **M.I. Boyanov**, G. Shodunke, C. Gura, Q. Jin, M. F. Kirk. "Influence of pH on the balance between methanogenesis and iron reduction", *Geobiology* 17:185-198 (2019)
Methanogenesis and iron reduction play major roles in determining global fluxes of greenhouse gases. Despite their importance, environmental factors that influence their interactions are poorly known. Here we present evidence that pH significantly influences the balance between each reaction in anoxic environments that contain ferric (oxyhydr)oxide minerals. In sediment bioreactors that contained goethite as a source of ferric iron, both iron reduction and methanogenesis occurred but the balance between them varied significantly with pH. Compared to acidic bioreactors, electron donor oxidation in alkaline bioreactors was 85% lower for iron reduction and 61% higher for methanogenesis. Thus, as pH increased, methanogenesis increasingly displaced iron reduction. Geochemistry data collected from U.S. aquifers demonstrate that a similar pattern also exists on a broad spatial scale in natural settings. In contrast, in bioreactors that were not augmented with goethite, clay minerals served as the source of ferric iron and the balance between each reaction did not vary significantly with pH. We therefore conclude that the availability of ferric (oxyhydr)oxide minerals influences the extent to which the balance between each reaction is sensitive to pH. The results of this study advance our understanding of environmental controls on microbial methane generation and provide a basis for using pH to refine predictions of greenhouse gas fluxes.

Q. Yu, **M.I. Boyanov**, J. Liu, **K. M. Kemner**, J. Fein. "Adsorption of selenite onto *Bacillus subtilis*: the overlooked role of cell envelope sulfhydryl sites in the microbial conversion of Se(IV)", *Environ.Sci.Tech* 52, 18, 10400-10407 (2018)
Microbial activities play a central role in the global cycling of selenium. Microorganisms can reduce, methylate and assimilate Se, controlling the transport and fate of Se in the environment. However, the mechanisms controlling these microbial activities are still poorly understood. In particular, it is unknown how the negatively-charged Se(IV) and Se(VI) oxyanions that dominate the aqueous Se speciation in oxidizing environments bind to negatively-charged microbial cell surfaces in order to become bioavailable. Here, we show that the adsorption of selenite onto Bacillus subtilis bacterial cells is controlled by cell envelope sulfhydryl sites. Once adsorbed onto the bacteria, selenite is reduced, and forms reduced organo-Se compounds (e.g., R1S-Se-SR2). Because sulfhydryl sites are present within cell envelopes of a wide range of bacterial species, sulfhydryl-controlled adsorption of selenite likely represents a general mechanism adopted by bacteria to make selenite bioavailable. Therefore, sulfhydryl binding of selenite likely occurs in a wide range of oxidized Se-bearing environments, and because it is followed by microbial conversion of selenite to other Se species, the process represents a crucial step in the global cycling of Se.

S. Yan, **M.I. Boyanov**, **B. Mishra**, **K.M. Kemner**, **E.J. O'Loughlin**. "U$^{VI}$ Reduction by biogenic and abiotic hydroxycarbonate green rusts: Impacts on U(IV) speciation and stability over time" *Environ.Sci.Tech*. 52 (2018) 4601–4609

Green rusts (GRs) are redox active Fe(II)-Fe(III) minerals that form in the environment via various biotic and abiotic processes. Although both biogenic (BioGR) and abiotic (ChemGR) GRs have been shown to reduce U(VI), the dynamics of the transformations and the speciation and stability of the resulting U(IV) phases are poorly understood. We used carbonate extraction and XAFS spectroscopy to investigate the products of U(VI) reduction by BioGR and ChemGR. The results show that both GRs can rapidly remove U(VI) from synthetic groundwater via reduction to U(IV). The initial products in the ChemGR system are solids-associated U(IV)-carbonate complexes that gradually transform to nanocrystalline uraninite over time, leading to a decrease in the proportion of carbonate-extractable U from ~95% to ~10%. In contrast, solid-phase U(IV) atoms in the BioGR system remain relatively extractable, non-uraninite U(IV) species over the same reaction period. The presence of calcium and carbonate in groundwater significantly increase the extractability of U(IV) in the BioGR system. These data provide new insights into the transformations of U under anoxic conditions in groundwater that contains calcium and carbonate, and have major implications for predicting uranium stability within redox dynamic environments and designing approaches for the remediation of uranium-contaminated groundwater.

**M. I. Boyanov**, **K. M. Kemner**, "Application of synchrotron x-ray absorption spectroscopy and microscopy techniques to the study of biogeochemical processes, Chapter in *Analytical Geomicrobiology: A Handbook of Instrumental Techniques*, Eds. Alessi D, Veeramani H, Kenney J., Cambridge University Press.

The need for increasingly detailed characterization of geomicrobiological or geochemical systems has necessitated the use of increasingly sophisticated analytical techniques that enable direct measurements of the atomic-scale parameters used in mechanistic models. From the characterization techniques available today, those utilizing penetrating x-rays have the distinct advantage of being able to probe environmental samples in their natural hydrated state, without the need for complicated sample preparation that could potentially alter the system and without the limitation of surface-only sensitivity that is typical of particle and optical probes. In addition, biogeochemical samples of interest are often noncrystalline and consist of many chemical components, which complicates their structural characterization by conventional techniques. In this chapter we discuss how the methods of synchrotron x-ray absorption spectroscopy (XANES and EXAFS) overcome many of these limitations to provide the chemically specific, molecular-scale information needed to unravel the mechanisms controlling biogeochemical processes. Current x-ray focusing technology is capable of providing hard x-ray beams in the nanometer size range, which enables the application of x-ray fluorescence (XRF) spectroscopy techniques at spatial resolutions comparable to those of scanning electron microscopy, but with approximately 1000-fold higher elemental sensitivity. These methods can be applied to a diverse range of environmental systems, such as adsorption of heavy metals to minerals, plants, or bacterial cells, redox transformations of metals and radionuclides induced by microbial activity, biomineralization, nanomineral nucleation and precipitation, metal uptake, transport, and distribution within biomass, and many other areas of biogeochemistry.

b. *Future scientific goals*

**FY2020**

- Conduct laboratory and greenhouse mesocosm studies to determine influence of pH and DOC on plaque and oxidized rhizosphere formation and their impact on U immobilization; prepare manuscript (RhKG1.1)
- Collect rhizosphere and bulk soil samples from contaminated portions of Tims Branch and characterize Fe mineralogy; prepare manuscript (Rh KG1.2)

- Collect rhizosphere and bulk soil samples from uncontaminated portion of Tims Branch and characterize the organic matter; prepare manuscript (Rh KG1.4)

- Finish ground surveys of U concentrations in the sediment at the Tims Branch field site; initiate aerial surveys for larger scale U maps of the site (Sd KG 1.1)

- Continue collecting sediment cores based on the results of U concentration surveys (Sd KG 1.1-1.4)

- Continue with characterization of samples from the sediment cores using synchrotron techniques to determine U speciation with depth and with core location (Sd KG 1.1)

- Characterize microbial composition to relate to the observed U speciation (Sd KG 1.1)

- Characterize elemental content and organic matter to relate them to the observed U valence state and speciation (Sd KG 1.1-1.2)

- Continue laboratory experiments and reactors with defined mineral-microbe assemblages; prepare manuscript(s) describing aspects of the effect of U:ligand ratio on $U^{IV}$ speciation (Sd KG 1.2)

- Prepare manuscript(s) reporting the results of the field surveys, the U speciation in the sediment, and the effect of environmental factors (e.g., ligand:U ratio, microbial composition and function, organic matter content, etc.) on U speciation  (Sd KG 1.1-1.2)

- Initiate controlled reoxidation experiments of $U^{IV}$ in the sediment samples to determine if $Fe^{II}$ in the reduced sediments hinders $U^{IV}$ reoxidation and remobilization; determine U and Fe valence by spectroscopic techniques (Sd KG 1.4, 2.1)

- Characterize U speciation in the colloidal fraction of the sediment by synchrotron techniques; initiate controlled laboratory experiments to determine the effect of organic matter and silicate on the sequestration of $U^{IV}$ in colloids (Sd KG 1.3)

- Initiate anoxic column experiments with SRS sediment to test whether U mobility under reducing conditions is controlled by colloidal transport (Sd KG 2.2)

- Continue routine observation and monitoring of stream flow, water chemistry, suspended solids (including incidents of floc formation), water table, near-stream sediment porewater, and meteorological data—with more aggressive sampling surrounding storm events (background information relevant to several hypotheses, particularly St KG2.1, and St KG2.2)

- Continue collection of Fe flocs for characterization of native microbial communities, elemental composition, Fe and U speciation, and carbon characterization (background information relevant to St KG 1.1, St KG 1.2, and St KG 2.3)

- Conclude batch reactor experiments investigating the potential role of IOB in the formation of Fe flocs in Tims Branch (St KG 1.1)

- Finish batch reactor experiments investigating the extent to which Fe flocs sequester and stabilize U (St KG 1.2)

- Conclude batch reactor experiments to examine the stability of U sequestered in Fe flocs under anoxic conditions (St KG 1.3)

- Prepare paper describing the native microbial communities, elemental composition, Fe and U speciation, and carbon characterization of Fe flocs (background information relevant to St KG 1.1, St KG 1.2, and St KG 2.3)

- Prepare paper detailing the role(s) of iron oxidizing and reducing bacteria in Fe floc formation and stability (St KG 1.1 and St KG 1.3)

- Conclude laboratory experiments examining the stability of colloidal U under controlled conditions representative of conditions in Tims Branch (St KG 2.1)

- Conduct Jar-tester experiments to determine the factors controlling the formation, stability and break up, and settling of Fe flocs (St KG 2.2)

*c. Scientific results that may shift current research focus and/or identify new knowledge gaps*

Results obtained to this point are on track with anticipated outcome and, in some cases, ahead of schedule.

We have been able to opportunistically take advantage of previously unknown radioactivity monitoring capabilities at SRNL. Specifically, we have made use of helicopter flyover efforts interfaced with NaI scintillator crystals to measure the near surface gamma ray emissions from the Tims Branch watershed to determine the distribution of radioactivity within the watershed with approximately 25 m spatial resolution. These mapping efforts have provided keen insights into optimal locations for field sampling with subsequent analysis of the field materials at the APS to determine U and Fe valence states and local chemical environments. In light of these new helicopter flyover results, additional gamma ray mapping is planned for FY20 with 1.5 m spatial resolution.

We have initiated new collaborations through the engagement of numerous university partners to broaden the scope of the Wetland Hydrobiogeochemistry SFA and bring in critical capabilities needed for the SFA. These efforts have resulted in 17 university-led proposal submissions to DOE BER FOA #0002035.

*d. Collaborative research activities with external researchers in pursuit of program objectives*

Integration of scientific and technical expertise, plus communication among all of the researchers who are part of the Argonne Wetland Hydrobiogeochemistry SFA, is critical for the success of the Argonne Wetland Hydrobiogeochemistry SFA science program. Active participation by external collaborators who are not directly funded by the Argonne SFA provides synergistic and complementary expertise essential to the productivity of the research program. The following activities between Argonne and external SFA researchers not directly funded by the SFA are worthy of note:

. Members of the Argonne SFA have been collaborating with Drs. Cara Santelli and Crystal Ng (University of Minnesota) on a 1-year exploratory research project within the uncontaminated zone of Tims Branch to investigate the importance of microbial sulfate reduction, its coupling to microbial iron reduction, and its effect on water quality within Tims Branch. Hydrological modeling and field monitoring expertise provided by Drs. Santelli and Ng have catalyzed the installation of multiple near surface and stream water level monitoring wells at the contaminated and uncontaminated field sites within the Tims Branch watershed.
. Members of the Argonne SFA have been collaborating with Dr. Martial Taillefert (Georgia Technology University) on a 1-year exploratory research project within the uncontaminated zone of Tims Branch to use electrochemical monitoring approaches to identify the importance of coupled biogeochemical cycling of Fe, S, and N and its effect on water quality within uncontaminated zones of Tims Branch.
. Members of the Argonne SFA have been collaborating with Drs. Jeff Catalano and Dan Giammar (Washington University, St. Louis) on a 3-year DOE BER SBR-supported research project to understand the role of trace metals in the control of methane production and consumption and the control of water quality in redox dynamic environments. Field sites being used for these studies include Tims Branch and the Argonne wetlands.
. Beginning in August 2018, a visiting scholar (Dr. Xiaoqin Nie) supported by and from Southwest University of Science and Technology, China began a 1-year sabbatical at Argonne with the members of the Argonne Wetland Hydrobiogeochemistry SFA to investigate the role of moss and Ca concentrations on the chemical speciation of uranium within Tims Branch sediments. This work is still ongoing. However, preliminary x-ray imaging and spectroscopy results have identified

significant active uptake of U by moss leaves. We expect at least one publication in FY20 to result from this work.

- Beginning in October 2018, a graduate student (Limin Zhang) supported by and from China University of Geoscience-Beijing joined members of the Argonne Wetland Hydrobiogeochemistry SFA through a long-standing collaboration with one of her co-advisors (Dr. Hailiang Dong) from Miami University of Ohio. During the six months that she worked in the Argonne SFA labs, Limin Zhang investigated the role of chelating agents in affecting the biogeochemical redox transformations of uranium. Results of this work were included in her dissertation and are presently being written up for publication.

- Beginning in November 2018, a graduate student (Tianliang Zheng) supported by and from China University of Geoscience-Wuhan joined members of the Argonne Wetland Hydrobiogeochemistry SFA for a 1-year focused research project. The emphasis of his research is on redox dynamic processes within wetlands at Argonne, Tims Branch at SRNL, and in China and the effect of redox transitions on contaminant metal chemical speciation. Recent anaerobic microbial sulfate reduction experiments performed by Tianlian Zheng at Argonne indicate redox-driven transformations of ferrihydrite. We expect at least one publication to result from this work in FY20 and FY21.

- Beginning in October 2018, a graduate student (Yanghao Shen) supported by and from School of Nuclear Science and Technology, Lanzhou University, China joined members of the Argonne Wetland Hydrobiogeochemistry SFA for a 2-year study program. Yanghao Shen is investigating the role of fungi in affecting the solid-solution partitioning of uranium as well as its chemical speciation. Depending upon the results of this work, we may initiate a survey of fungi within Tims Branch and investigate the role of those fungi in affecting water quality within Tims Branch watershed.

- Since the fall of 2018, Dr. Brian Powell (Clemson University), while being supported by an EPSCoR grant, has worked with members of the Argonne SFA to map U concentrations in Tims Branch, initiate the development of multiple RTMs across scales, and develop novel imaging techniques to monitor water flow and reactivity.

- During FY19 Drs. Hess and Pasa-Tolic (PNNL) have worked with members of the Argonne SFA to optimize the use of EMSL technologies to characterize C chemistries within sediment and water samples collected from the Tims Branch watershed. Preliminary FTICR-MS data have been collected on a series of samples from gaining and losing regions of Tims Branch. Results from these studies will be used in the submission of a full proposal to EMSL in the fall.

- A graduate student (Juan Morales) from Florida International University, through SFA collaborator Dr. Lawrence (Florida International University), joined members of the Argonne Wetland Hydrobiogeochemistry SFA for a 10-week summer study program. Juan Morales has extensive knowledge of the Tims Branch watershed through his work at Florida International University with Dr. Lawrence and is investigating the use of microbial community structure as a sentinel for Sn and Hg water contamination.

- Dr. Man-Jae Kwon, a research scientist at the Korean Institute of Science and Technology (KIST) Gangneun, has continued an active no-cost collaboration with the Argonne SBR SFA. He works closely with Drs. O'Loughlin, Boyanov, and Kemner on projects of mutual interest involving Fe and S biogeochemistry.

- Drs. O'Loughlin, Boyanov, and Kemner continue to work closely with Dr. Sen Yan, an Assistant Professor in the Department of Geochemistry at the China University of Geosciences-Wuhan. As a visiting scholar at Argonne in 2015, Dr. Yan worked with the Argonne SBR SFA team to investigate U(VI) interactions with biotic and abiotic green rusts. That work was recently published (S. Yan, M. I. Boyanov, B. Mishra, K. M. Kemner, E. J. O'Loughlin, "U(VI) reduction by biogenic and abiotic hydroxycarbonate green rusts: Impacts on U(IV) speciation and stability over time," *Environ. Sci. Technol.*, **52** 4601-4609 2018. DOI 10.1021/acs.est.7b06405).

- Dr. Renata Rodrigues (Universidade Federal de Alfenas), a professor at and supported by Universidade Federal in Brazil, and one of her graduate students, spent a year (September 2017-September 2018) on sabbatical working in the Argonne Biogeochemistry labs to investigate effects of pH and sulfate concentration on heavy metal valence states in samples from bioreactor experiments

that simulate bioremediation treatment procedures. She is also beginning flocculation experiments in her labs in Brazil to investigate controls on colloid formation. Another one of her graduate students will be joining SFA researchers at Argonne in the fall of 2019 to set up flocculation and colloid formation experiments in the Argonne Biogeochemistry labs.

. Drs. Adams, Arkin, and Charaborty (LBNL) and Henry (Argonne) have collaborated with Dr. Weisenhorn and other Argonne SFA team members to develop new applications within KBase that will enable analysis of microbial interaction networks to determine the importance of those interactions networks in controlling water quality in Tims Branch.

. For more than 20 years, Dr. Segre (Illinois Institute of Technology) has provided expertise and oversight related to the daily operation of the MRCAT/EnviroCAT at the APS.

. In FY19, members of the Argonne SFA and the university-led project at the University of Minnesota have worked with Dr. James Stegen (PNNL) to include analysis of Tims Branch water samples within the WHONDRS project.

## 5) Staffing and budget summary

*a/b. Allocation by program tasks and to support external collaborations*

The allocation of FY2019 funds is shown below.

| Institution | FY2019 Funding ($K) | Status FY2020 ($K) |
|---|---|---|
| Argonne | | |
| Kemner (PI) | 300 | Active (300) |
| O'Loughlin (Co-PI, Stream) | 300 | Active (300) |
| Weisenhorn | 50 | Active (50) |
| Dan Kaplan- Savannah River National Laboratory (separate FWP)- (Rhizosphere) | 150 | (150) |
| Boyanov- Bulgarian Academy of Science- (Sediment) | 165 | Active (165) |
| Illinois Institute of Technology (MRCAT/EnviroCAT) | 215 | Active (165)[1] |

[1]The subcontract to IIT to cover beam line support will be decreased from $150K (FY19) to $100K (FY20). Additional funds to IIT are to cover part time efforts of Deirdre Sholto-Douglas (Microbiologist and lab technician for Argonne SFA).

*c. Personnel actions and procedures*

Argonne Wetland Hydrobiogeochemistry SFA staffing changes that occurred or will occur in FY2019 include the following: Dr. Dion Antonopoulos replaced Dr. Philippe Noirot on June 10, 2019 as Director of the Argonne Bioscience Division. Presently, Dr. Antonopoulos is listed as the interim Bioscience Division Director. Dr. Antonopoulos was a member of the Argonne SBR SFA during FY2013-FY2018 and continues to have a good collaborative working relationship with members of the Argonne SFA. In addition, Dr. Robin Graham has announced her intention to retire before the end of FY19. Should her position of Deputy Associate Laboratory Director not be filled, we envision Dr. Christina Negri (Argonne Environmental Science Division Director) taking on some of the responsibilities that were described above in this section for the Deputy Associate Laboratory Director. Members of the SFA will work closely with both the Bioscience Interim Division Director (Dr. Antonopoulos) and the Environmental Science Division Director (Dr. Negri) to maintain communication between DOE BER and the Argonne SFA, optimize synergies between the SFA and new research initiatives at Argonne, and to advance the

SFA. Dr. Weisenhorn effort's on the SFA will be reduce from 25% (FY2019) to 15% (FY2020) unless additional funds beyond the $50K provided in FY2019 are allocated from DOE BER.

*d. National Laboratory investment in the program*

In FY2017 and FY2018 Dr. Weisenhorn has been supported with Argonne LDRD funds (Integrating Atmospheric, Ecological, and Biogeochemical Monitoring in Wetlands). Drs. O'Loughlin and Kemner also received support from the same LDRD. Argonne provided $50K of support in FY2016 to a project entitled "Developing Remote Automated Sensors to Direct Sampling of Aerobic-Anaerobic Switching in Floodplain Ecosystems" that included support for Dr. O'Loughlin.

Argonne is presently providing LDRD funds ($300K/year) in FY19-FY21 to Dr. Weisenhorn and collaborators to work on an LDRD entitled "The Importance of Soil Water Content Heterogeneity for Determining Landscape Level Processes." One of the objectives of this LDRD is to develop a conceptual framework and a testbed to understand the spatial and temporal scales at which soil moisture heterogeneity operates and its effects on land-atmosphere fluxes of water, carbon, and energy at the landscape level. An additional goal is to initiate collaborative interactions between members of the Argonne SBR SFA, the Argonne TES SFA, and E3SM research efforts located at Argonne. Although not receiving support from this LDRD, Drs. O'Loughlin and Kemner participate in bi-monthly meetings to keep abreast of the research progress and explore opportunities to integrate SBR interests in the research.

*Capital Equipment needs (FY2020)*

$190K is requested for a variety of needs related to lab and field research. Items include an XRD powder diffractometer ($84K), GPS signal booster ($1.4K), water quality multiparameter probe ($10K), pressure transducers for later level monitoring ($10K), soil moisture probe ($7.2K), LGR gas monitor ($65K), and a Hach Kit ($7.5K).

**Appendix A. Manuscripts published, in press, or in review, since submission of last Science Plan (Authors in bold are Argonne SFA members)**

**Peer-reviewed Publications:**

1. M. E. Bishop, H. Dong, P. Glasser, B. R. Briggs, M. Pentrak, J. W. Stucki, **M. Boyanov**, **K. M. Kemner**, L. Kovarik, "Reactivity of redox cycled Fe-bearing sediments towards hexavalent chromium reduction", *Geochimica et Cosmochimica Acta* 252 (2019) 88–106
2. K.A. Marquart, B.R. Haller, J.M. Paper, **T.M. Flynn**, **M.I. Boyanov**, G. Shodunke, C. Gura, Q. Jin, M. F. Kirk. "Influence of pH on the balance between methanogenesis and iron reduction", *Geobiology* 17:185-198 (2019)
3. Q. Yu, **M.I. Boyanov**, J. Liu, **K. M. Kemner**, J. Fein. "Adsorption of selenite onto *Bacillus subtilis*: the overlooked role of cell envelope sulfhydryl sites in the microbial conversion of Se(IV)", *Environ.Sci.Tech* 52, 18, 10400-10407 (2018)
4. S. Yan, **M.I. Boyanov**, **B. Mishra**, **K.M. Kemner**, **E.J. O'Loughlin**. "$U^{VI}$ reduction by biogenic and abiotic hydroxycarbonate green rusts: Impacts on U(IV) speciation and stability over time" *Environ.Sci.Tech*. 52 (2018) 4601–4609
5. Zheng T, Deng Y, Wang Y, Jiang H, **Flynn TM**, **O'Loughlin EJ**, Gan Y, Ma T "Seasonal variation of microbial community in arsenic-rich alluvial aquifer systems: Response to groundwater level fluctuation" Journal of Hazardous Materials, Vol. 367, p. 109–119. doi: 10.1016/j.jhazmat.2018.12.087.

**Manuscripts in Review:**

1. **O'Loughlin, E. J**., C. Gorski, **T. M. Flynn**, and M. M. Scherer. Effects of electron donors on the formation of secondary mineralization products resulting from the bioreduction of lepidocrocite by *Shewanella putrefaciens* CN32. *Minerals*.

2. **M. I. Boyanov, K. M. Kemner**, "Application of synchrotron x-ray absorption spectroscopy and microscopy techniques to the study of biogeochemical processes, Chapter in *Analytical Geomicrobiology: A Handbook of Instrumental Techniques*, Eds. Alessi D, Veeramani H, Kenney J., Cambridge University Press. (accepted)

**Appendix B. Scientific Presentations since submission of last Science Plan**

**Invited Presentations: (Presenting author is underlined)**

1. B. L. Huhmann, K.A. Rothwell, **M. I. Boyanov**, **K.M. Kemner**, M. M. Scherer, A. Neumann. "Reactions at the Fe mineral-water interface: Impact on contaminant fate," ACS Fall 2018, Boston, August 19, 2018
2. C.R. Johnson, D.A. Antonopolous, **M. Boyanov**, **T. Flynn**, J.C. Koval, **K.M. Kemner**, **E.J. O'Loughlin**, "Reduction of antimony(V) by coupled biotic and abiotic processes under sulfidogenic conditions", Annual Meeting of the Society for Industrial Microbiology and Biotechnology, Hilton Chicago, IL, August 12-16, 2018
3. **K. Kemner**, **M. Boyanov**, D. Latta, **B. Mishra**, **E. O'Loughlin**, M. Scherer, S.Yan. "Redox dynamic iron mineralogy and its effect on uranium transformations", Session on "Redox & Interfacial Dynamics Among Coupled Biogeochemical Cycles of Fe, S, Minerals & Organic Matter: Implications to Multiscale Behaviors of Contaminants, Carbon & Nutrients", Spring ACS Meeting, New Orleans, March 19, 2018
4. **Catalano J.G.**, Crompton N.M., Bradley A.S., **Giammar D.E.**, Hasenmueller E.A., and Chambers L.G. "Link between Metal Speciation and Biogeochemical Processes in Wetland Soils." 15th International Conference on the Biogeochemistry of Trace Elements, Nanjing, China. May 5 - 9, 2019. (Keynote presentation)
5. **Catalano J.G.** "Trace Metal Limitations on Methane Production in Freshwater Wetlands." China University of Geosciences, Wuhan, China. May 14, 2019.
6. **Flynn TM**, Sladek M, Jensvold Z, Marshall C, Antonopoulos D, Koval J, **Kemner K**, **O'Loughlin E** "Impact of electron shuttles on wetland soil microcosms," Society for Industrial Microbiology and Biotechnology Annual Meeting, Chicago, IL, August 2018.
7. **Flynn TM** "Microbes, metals, and minerals: Shuttling electrons around in the subsurface," China University of Geosciences, Wuhan, China, June 2018.
8. **Flynn TM** "Microbial pathways of organic carbon utilization," ESS PI Meeting, Potomac, MD, May 2018.
9. **Kaplan, D. I., M. Boyanov, K. Kemner, E. O'Loughlin, P. Weisenhorn**. 2019. Uranium Biogeochemistry in the Rhizosphere of the Tims Branch Wetland: Research Opportunities. Florida International University, February 13, 2019.
10. **Kaplan, D. I**. 2019. Uranium in Savannah River Site's Wetlands. Laboratory Director's Technical Exchange Seminar Series. Savannah River National Laboratory, Aiken, SC. May 5, 2019.
11. **Kaplan, D. I**., R. J. Smith, M. Baker, B. O. Ferguson, **N. E. Martinez**, D. A. Montgomery, C. Parker, **J.C. Seaman**, **B. A. Powell**, **M. Boyanov**, **E. J. O'Loughlin**, and **K. M. Kemner**. Uranium Remobilization form a Wetland 50 Years After Contamination. Goldschmidt Conference, Barcelona, Spain, August 18-23, 2019.
12. **K. M. Kemner**, "X-ray tomographic investigations of the distributions of bacteria within soil aggregates," Combined DXC & ICXOM. 25 Conference, Lombard, Illinois, August 5-9, 2019.
13. **K. M. Kemner**, "Using a synchrotron for Biological and Environmental Research: Taking Superman's x-ray vision to a new level," West Virginia University Department of Forestry, March 22, 2019.
14. **K. M. Kemner**, "Micro and nanotomographic investigations of soil aggregate microbial and pore structure," Marine Biology Laboratory Remote Presentation Series, February 14, 2019.
15. **K. M. Kemner**, S. O'Brien, M. D. Whiteside, D. Sholto-Douglas, O. Antipova, M. I. Boyanov, A. Dohnalkova, D. Gursoy, L. Kovarik, B. Lai, C. Roehrig, C. Soriano Hoyuelos, S. Sullivan, S. Vogt, "Micro and nanotomographic investigations of microbial and pore structure within opaque soil aggregates," Ecological Society of America Annual Meeting, New Orleans, Louisiana, August 6-11, 2018.

16. **<u>K. M. Kemner</u>**, "Lab- and field-based approaches to facilitate microbial modeling of hydrobiogeochemical processes," US DOE ESS Annual PI Meeting, Reston, Virginia, May 1, 2018.
17. **<u>K. M. Kemner</u>**, M. I. Boyanov, E. J. O'Loughlin, T. Flynn, "Understanding processes that drive Coupled iron, carbon, and uranium Hydrobiogeochemistry," Louisiana State University, Baton Rouge, Louisiana, March 16, 2018.
18. **<u>P. Weisenhorn</u>**. "Tracking changes in microbial interactions through time." Argonne LDRD Seminar Series, May 22, 2018.
19. **<u>P. Weisenhorn</u>**, J.F. Lopes, J. Edirisinghe, R. Taylor, D. VanDerLelie, H.S. Song, H. Bernstein, J. Zucker, S. Lindemann, C.S. Henry. "Community metabolic modeling reveals common auxotrophies across a variety of microbiome systems." American Society of Microbiology annual meeting, June 2018.
20. **<u>P. Weisenhorn</u>**, **T. Flynn**, **M. Boyanov**, **D. Kaplan**, **C. Henry, K. Kemner, E. J. O'Loughlin**. "Microbiome heterogeneity across the redox dynamic zone." American Geophysicists Union annual meeting, Dec. 2018.
21. **<u>P. Weisenhorn</u>**, **T. Flynn, M. Boyanov, D. Kaplan, C. Henry, K. Kemner, E.J. O'Loughlin**. "Microbiome heterogeneity across the redox dynamic zone." DOE Genomic Sciences PI meeting, Feb. 2019.
22. **<u>P. Weisenhorn</u>**. "Plant-microbe interactions across scales" Dept. Plant Biology, Southern Illinois University, Carbondale. March 8, 2019.
23. **<u>P. Weisenhorn</u>**, **C. Meile**, R. Versteeg, Q. Zhang, T. Gu, J. Edirisinghe, **K. Kemner, C.S. Henry**. "Integrating biological processes into reactive transport models with DOE's Systems Biology Knowledgebase (KBase)." MODFLOW and More meeting, Denver, Colorado, June 2019.
24. **<u>O'Loughlin, E. J.</u>** 2018. Products of microbial Fe(III) oxide reduction: Magnetite versus green rust, China University of Geosciences, June 19, Wuhan, China.
25. **<u>O'Loughlin, E. J</u>**. 2018. Cycling of Major/Minor Elements and the Fate and Transport of Contaminants in Natural Systems, *Governors State University,* April 12, University Park, IL.

**Contributed Presentations: (Presenting author is underlined)**

1. **Boyanov MI**, **O'Loughlin EJ**, **Weisenhorn P**, **Flynn TM**, **Kaplan DI**, **Powell B**, **Martinez N, Shen Y, Nie X, Zhang L, Dong H, Kemner KM.** "Savannah River Site Sediments: Biogeochemistry and U speciation", Environmental System Science Principal Investigator (PI) Meeting, Potomac, MD. April 29 - May 1, 2019

2. <u>**Weisenhorn P, Meile C, Kaplan DI, O'Loughlin EJ, Boyanov MI, Zhang Q, Gu T, Powell B, Flynn TM, Henry C, Kemner KM**</u>. "Modeling Microbial Controls on Biogeochemical Processes at the Savannah River Site", Environmental System Science Principal Investigator (PI) Meeting, Potomac, MD. April 29 - May 1, 2019

3. <u>**Santelli CM, Ng C, Dunshee A, Rosenfeld C, Kaplan D, Kemner K, O'Loughlin EJ, Weisenhorn P, Boyanov M.**</u> "Influence of Hyporheic Exchange on Coupled S-Fe-C Biogeochemical Cycling in Riparian Wetland Sediments", Environmental System Science Principal Investigator (PI) Meeting, Potomac, MD. April 29 - May 1, 2019

4. <u>**O'Loughlin EJ, Boyanov MI, Kaplan DI, Orlandini K, Weisenhorn P, Kemner KM**</u>. "Iron Flocs as Biogeochemically Dynamic Reservoirs of Uranium in Tims Branch Wetlands, Savannah River Site", Environmental System Science Principal Investigator (PI) Meeting, Potomac, MD. April 29 - May 1, 2019

5. <u>**Kemner KM, Weisenhorn P, Boyanov MI, Kaplan DI, Seaman J, Li D, Powell B, Mahmoudi M, Lawrence A, Flynn TM, Kwon M-J, Yan S, Wang Y, Deng Y, Dong Y, Hess N, Pasa-Tolic L, Rodriguez R, Segre C, Mishra B, Chakraborty R, Adams P, Arkin A, Santelli C, Ng C, Taillefert M, Catalano J, Giammar D, Meile C, O'Loughlin EJ.**</u> "Argonne Wetland Hydrobiogeochemistry SFA", Environmental System Science Principal Investigator (PI) Meeting, Potomac, MD. April 29 - May 1, 2019

6. <u>**M. Boyanov**</u>**, E. O'Loughlin, D. Kaplan, K. Kemner.** "The utility of EXAFS in discovering novel species relevant to U mobility in reducing environments", The international XAFS2018 conference, Krakow, Poland, July 22-27, 2018

7. <u>B. Ham</u>, J. Kwon, **M.I. Boyanov**, **K.M. Kemner**, **M.-J. Kwon**, "Geochemical and microbial characteristics of waste disposal sites affected by seawater intrusion and high alkalinity", Session on "Microbial interactions with minerals and metals", Goldschmidt2018, Boston, August 13, 2018

8. <u>Q. Yu</u>, **M.I. Boyanov**, J. Liu, **K.M. Kemner**, J.B. Fein, "Adsorption of selenite by *Bacillus subtilis*: the overlooked role of cell envelope sulfhydryl sites in microbial conversion of Se(IV)", Session on "Biogeochemistry of Oxyanion-forming Elements: the Good, the Bad and the Ugly", Goldschmidt2018, Boston, August 13, 2018

9. <u>**M. Boyanov**</u>, D. Latta, M. Scherrer, B. Mishra, B. Huhmann, A. Neumann, **E. O'Loughlin**, **K. Kemner**. "Redox Transformations of U, Hg, and As in Iron Oxide and Clay Systems ", Environmental System Science Principal Investigator (PI) Meeting, Potomac, MD. May 1-2, 2018

10. <u>**E. O'Loughlin**</u>**, M. Boyanov, T. Flynn, D. Kaplan, B. Powell, P. Weisenhorn, K. Kemner**. "Elemental Content, U Redox Dynamics, and Microbial Communities in Wetland Sediment Cores from Tims Branch, Savannah River Site ", Environmental System Science Principal Investigator (PI) Meeting, Potomac, MD. May 1-2, 2018

11. <u>**T. Flynn**</u>, L. Johnson, Z. Jensvold, M**. Boyanov**, **K. Kemner**, **E. O'Loughlin**, "Effects of Fe(III) Inputs on the Rate of Methanogenesis inWetland Sediment Microcosms", Environmental System Science Principal Investigator (PI) Meeting, Potomac, MD. May 1-2, 2018

12. <u>**Kemner KM**</u>, Antonopoulos DA, **Flynn TM**, **Henry C, Weisenhorn P, Boyanov MI, Mishra B, Segre C**, Latta DE, Scherer MM, **Kaplan D, Li D, Martinez N, Moysey S, Powell B, Rodriguez R, Kwon M-J, Yan S, Adams P, Chakraborty R, Tfaily M, O'Loughlin EJ**, "The Argonne National Laboratory Subsurface Biogeochemical Research Program SFA:

Wetland Hydrobiogeochemistry", Environmental System Science Principal Investigator (PI) Meeting, Potomac, MD. May 1-2, 2018

13. M. Ramos, **M. Boyanov**, **K. Kemner**, **E. O'Loughlin**, "Bioreduction of iron in pyroaurite by *Shewanella putrefaciens* CN32", Session on "General Geochemistry", Spring ACS Meeting, New Orleans, March 21, 2018

14. K. Thalhammer, **M. Boyanov**, **K. Kemner**, **E. O'Loughlin**, "Reduction of Hg(II) by structural Fe(II) in clay minerals", Session on "Contaminated Site Remediation through Microbial, Geological & Chemical Processes", Spring ACS Meeting, New Orleans, March 21, 2018

15. **Boyanov M**, Latta D, **Mishra B**, Scherer M, **Yan S, O'Loughlin E, Kemner K**, "U(VI) and Fe-containing oxyhydroxide and clay minerals: Redox reactivity and products", Session on "Mineral-Water Interface Geochemistry & Modeling at the Laboratory- & Field-Scales", Spring ACS Meeting, New Orleans, March 19, 2018

16. Kirk MF, Jin Q, **Flynn TM**, Zeglin LH "pH dependent interactions between iron reduction and methanogenesis suggest a new model for methanogenesis," Geological Society of America Annual Meeting, Indianapolis, IN, November 2018.

17. Casar CP, Osburn MR, **Flynn TM**, Masterson AL, Kruger BR (2018) "Mineral-hosted biofilm communities in the continental deep subsurface," International Society for Microbial Electrochemistry and Technology Meeting, St. Paul, MN, October 2018.

18. Kirk MF, Marquart KA, Paper JM, Haller BR, Shodunke G, **Flynn TM**, Jin Q, (2018) "pH-dependent interaction between iron reducers and methanogens and its impact on carbon budgets," South-Central Section of the Geological Society of America, 5d Annual Meeting, Little Rock, AR, March 2018.

19. **K. M. Kemner**, "Argonne Wetland Hydrobiogeochemistry SFA," Pacific Northwest National Laboratory Brown Bag Seminar, Richland, WA, May 6, 2019.

20. **K. M. Kemner**, "Demystifying the Synchrotron Experience," US DOE BER CESD PI meeting, Washington, DC, April 30-May 1, 2019.

21. **K. M. Kemner**, J. Bargar, P. Nico, H. Holman, R. Tappero, "U. S. Synchrotron Capabilities for Environmental System Science," US DOE BER CESD PI meeting, Washington, DC, April 30-May 1, 2019.

22. **P. Weisenhorn, T. Flynn, M. Boyanov, C. Henry, K. M. Kemner, E. J. O'Loughlin**, "Microbiome heterogeneity across the redox dynamic zone," American Geophysical Union Meeting, Washington, DC., December 9-14, 2018.

23. **P. Weisenhorn, E. J. O'Loughlin**, S. O'Brien, C. Marshall, **K. M. Kemner, T. Flynn**, "Seasonal variation shines the light on microbial community interactions," Society of Wetland Scientists Annual Meeting, Denver, Co., May 29 – June 1, 2018.

24. S. Molins, I. Ozgen, D. Dwivedi, Z. Xu, D. Svyatskiy, D. Livingston, D. Moulton, C. Steefel, K. Maher, **P. Weisenhorn**, M. Zavarin. "IDEAS-Watersheds: Partnership with the Watershed Function SFA and Fine-Scale Reaction Network Activities." DOE Environmental System Sciences PI meeting, April 2019.

25. **Flynn, T. M.,** L. Johnson, Z. Jensvold, **M. I. Boyanov, K. M. Kemner**, and **E. J. O'Loughlin**. 2018. Effects of Fe(III) inputs on the rate of methanogenesis in wetland sediment microcosms. *2018 Midwest Geobiology Symposium*, October 6, Evanston, IL.

26. **Flynn, T. M**., M. F. Sladek, Z. Jensvold, C. W. Marshall, D. A. Antonopoulos, J. C. Koval, **K. M. Kemner**, and **E. J. O'Loughlin**. 2018. Impact of electron shuttles on wetland soil microcosms. *Society for Industrial Microbiology and Biotechnology 2018 Annual Meeting and Exhibition*, August 13-16, Chicago, IL.

27. Kolb, S. A, **E. J. O'Loughlin**, and T. C. Gsell. 2018. Isolation and characterization of phthalate-degrading bacteria from Asian carp microbiomes and riverine sediments. *ASM Microbe*, June 6-11, Atlanta, GA.