



# Environmental System Science

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## Summary of projects awarded in summer 2016 under Funding Opportunity Announcement DE-FOA-0001437.

### Program Overview

The goal of the Environmental System Science (ESS) activity in the U.S. Department of Energy's Office of Science, Office of Biological and Environmental Research (BER) is to advance a robust predictive understanding of terrestrial environments, extending from bedrock to the top of the vegetated canopy and from molecular to global scales in support of DOE's energy and environmental missions. Using an iterative approach to model-driven experimentation and observation, interdisciplinary teams of scientists work to unravel the coupled physical, chemical and biological processes that control the structure and functioning of terrestrial ecosystems across vast spatial and temporal scales. State-of-science understanding is captured in conceptual theories and models which can be translated into a hierarchy of computational components and used to predict the system response to perturbations caused, for example, by changes in climate, land use/cover or contaminant loading. Basic understanding of the system structure and function is advanced through this iterative cycle of experimentation and observation by targeting key system components and processes that are suspected to most limit the predictive skill of the models. The ESS activity is comprised of the Terrestrial Ecosystem Science (TES) and the Subsurface Biogeochemical Research (SBR) programs.

### Funding Opportunity Announcement Overview

The Funding Opportunity Announcement **DE-FOA-0001437**, was jointly issued by the Terrestrial Ecosystem Sciences and Subsurface Biogeochemical Research programs and was released in the fall of 2015. The goal of this FOA was to improve the representation of

terrestrial ecosystem and/or subsurface processes, with a view toward capturing scientific understanding in conceptual theories and models that could be translated into a hierarchy of computational components and used to predict the system response to perturbations caused, for example, by changes in climate, land use/cover or contaminant loading. Applications to this FOA were expected to take a systems approach to understand ecosystems over the multiple temporal and spatial scales that are represented in models (e.g., single process models, ecosystem models, and global models such as the Community Earth System Model and the Accelerated Climate Model for Energy). This emphasis on the capture of advanced understanding in models had two goals. First, it sought to improve the representation of these processes in coupled models, thereby increasing the sophistication of the projections from those models. Second, it encouraged the community to understand and use existing models and to compare model results against observations or other data sets to inform future research directions. It also sought to encourage an iterative dialog between the process and modeling research communities such that research objectives would be designed to address model needs and that modeling efforts are designed to inform process research.

Overall, the FOA considered research applications that focused on measurements, experiments, modeling or synthesis to provide improved quantitative and predictive understanding of terrestrial ecosystem and/or subsurface processes that can affect the cycling and transport of carbon, water, nutrients, and contaminants. All projects were required to clearly delineate an integrative, hypothesis-driven approach and clearly describe the existing needs/gaps in state-of-the-art models. Applicants were required to provide details on

how the results of the proposed research, if successful, would be incorporated into numerical models of subsurface systems and/or terrestrial ecosystems. While the TES and SBR programs support a broad spectrum of fundamental research in environmental system science and considered research applications within this scope, this FOA particularly encouraged applications in the following Science Areas:

Science Area 1 – Belowground Processes: The role of belowground processes and mechanisms associated with a changing climate at ecologically relevant temporal and spatial scales;

- Processes and mechanisms for the mediation and transformation, mineralization, and stability of carbon in soils (e.g., including microbial cycling, mineral-organic interactions, soil organic matter accessibility); and/or
- Plant-Microbe-Soil interactions (e.g., mycorrhizal interactions; rhizodeposition) that mediate carbon flux and can extend to ecosystem carbon balance.

Science Area 2 – Critical Ecosystems: New or improved understanding of biogeochemical pathways (e.g., N and/or P) that mediate carbon feedbacks and ecosystem function in:

- Process and mechanisms that mediate carbon relevant biogeochemical processes in Arctic (including high latitude boreal forest) ecosystems; and/or
- Processes and mechanisms that mediate key climate feedbacks of tropical forests

Science Area 3 – Hydrobiogeochemistry and Ecohydrology

- Methodologies for quantitative measurements of exchange and flux rates (water and solutes) from the groundwater-surface water interaction zone at the local, reach, and watershed scales.
- Ecohydrological studies that enable tracking the fluxes, stocks, and transformations of key constituents that control the speciation, distribution, and bioavailability of inorganic elements, including oxygen, nutrients, particulates, and dissolved organic matter to enable systems-level understanding of groundwater/surface water/vegetation interactions.
- Influence of plant-microbe-soil interactions

on inorganic element cycling and transformation in the groundwater-surface water interaction zone.

- Multi-scale, facies-based, hydro-biogeochemical models of the groundwater-surface water interaction zone.
- Characterization and modeling of the spatial heterogeneity (physical, chemical and biologic) of subsurface, riverine/hyporheic, and terrestrial environments (including microbial community composition and function) and their impacts on groundwater-surface water exchange and biogeochemical reactive transport.
- Mechanistically-based multiscale modeling of coupled hydrologic, geochemical and biological processes in compartments and for the system as a whole.

Science Area 4 – Biogeochemistry

- Understanding of coupled redox dynamics among Fe and S cycles and organic matter/mineral dynamics and their subsequent roles in carbon, contaminant, and nutrient cycling.
- Investigation of the role of nitrogen species (e.g.,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{N}_2\text{O}$ ) in effecting electron transfer to/from Fe-containing minerals (e.g., oxides and clays), and subsequent mineralization processes.
- Structures and thermodynamics of model U(IV)-ligand complexes.
- Contributions to multi-scale mechanistic/reactive transport modeling of molecular scale processes that control inorganic element cycles and contaminant transport. Processes of interest include homogeneous precipitation of inorganic contaminants; co-precipitation of inorganic contaminants with minerals; ternary organic and inorganic element/contaminant surface complexes; diffusion and advection processes of inorganic elements/contaminants; and colloidal transport of inorganic elements/contaminants. Interfaces with sharp redox gradients are of particular interest. Multi-scale models are sought that bridge molecular to pore to core to plot to field and to watershed length scales.
- Characterization of microbial and molecular mechanisms (gene identity, proteins and their structure-function, and pathways of importance) of biogeochemical processes,

including nutrient, N- and C- cycling, biogenic gas formation and contaminant transformations in the subsurface and in groundwater-surface water interaction zones.

- Controls on the import and export of inorganic elements (e.g., Hg) from cells, including molecular-level imaging and characterization of cell surface functional properties and receptors for binding; identification of the cellular transport pathways involved in the uptake of the element; molecular-level experimental characterization of the mechanisms involved in intracellular transformation of elements; and mechanistic modeling of inorganic element transfer across critical biotic and abiotic interfaces.
- Contributions to multi-scale mechanistic/reactive transport models of microbial interactions with inorganic elements/contaminants and mineral surfaces.

Overall, proposed research was intended to fill critical knowledge gaps, including the exploration of high-risk approaches. BER encouraged the submission of innovative exploratory applications with potential for future high impact on terrestrial ecosystem and subsurface biogeochemical research.

16 awards (7 of which were exploratory awards) were made through this Funding Opportunity Announcement, totaling \$5,954,332 over one to three years.

### **Funded Projects**

#### **Terrestrial Ecosystem Sciences (TES)**

##### ***Resolving Conflicting Physical and Biochemical Feedbacks to Climate in Response to Long-Term Warming***

- **Principle Investigator:** Kristen DeAngelis (University of Massachusetts Amherst)
- **Collaborators:** Jerry Melillo (Marine Biological Laboratories); Bhoopesh Mishra (Illinois Institute of Technology University); Ken Kemner (Argonne National Laboratory); Serita Frey (University of New Hampshire)
- **Total Award:** \$600,000 over 3 years
- **Award Number:** DE-SC0016571

The acceleration of global warming due to terrestrial carbon (C)-cycle feedbacks is likely to be an important, though poorly defined, component of future climate change. Both the sign and magnitude of these feedbacks in the real Earth system are still highly uncertain due to gaps in basic understanding of terrestrial ecosystem processes. This research takes advantage of an ongoing long-term soil warming experiment in which soils at the Harvard Forest LTER in Massachusetts have been heated for 24 years. By examining this long-term climate warming manipulation, this research targets two of the biggest questions in soil carbon response to climate warming: how will carbon use efficiency and physical protection of carbon altered in a warming world?

Long-term warming has caused the soil system to act as a positive feedback to climate, but our studies show microbes acting to promote negative feedbacks to climate. Over 24 years of warming has resulted in a 16% loss of the soil C in the top 60 cm of the soil, with a quarter of this loss happening in the last 5 years. This positive feedback is in contrast to evidence that microbes are promoting negative feedbacks, including increased simple (monomeric) C use efficiency (CUE) in heated compared to control plots, reduced microbial biomass, and thermal acclimation of microbial respiration. In other systems, CUE of complex C, which requires extracellular processing, tends to be lower than that for simple C. To account for the increased C lost as CO<sub>2</sub> with long-term warming, we expect to find that warming has little effect on the CUE of simple C, but that warming has decreased the CUE of complex C, which may account for the large loss of soil C over time.

Physical protection is afforded to SOM by adhesion to mineral surfaces as well as by occlusion in aggregates, and these experiments will quantify both. We have also observed altered physical protection with long-term warming, where the SOM pool in the mineral soil is less processed in the heated compared to control plots. We expect that long-term warming has altered the spatial distribution of SOM and its association with minerals such that soil C in heated plots is less physically protected and more available to microbial degradation and subsequent mineralization to CO<sub>2</sub>.

The goal of this research is to quantify the relative importance of, and interactions between, changing physical protection of soil C and CUE over long-term warming. This study focuses on soils collected from the long-term warming experiment at the Harvard Forest LTER in central Massachusetts, where soils have been heated 5°C above ambient continuously since 1991. We propose work in three objectives to understand the continued loss of soil C over the course of long-term warming: (1) Quantify long-term warming effects on physical protection of C in SOM. Our hypothesis is that long-term warming has resulted in a decrease in physical protection of SOM, making soil C in heated soils more temperature sensitive relative to controls. (2) Test organic C monomers, dimers, and polymers that require extracellular processing to establish whether long-term warming lowers CUE of more complex C. We predict reduced CUE of complex C sources (cellulose, chitin) in warmed compared to control soils, attenuated treatment effect for dimers, and no difference for monomers. (3) Quantify the contributions of CUE and physical protection to C cycling by incorporating them into the Microbial-Mineral Carbon Stabilization (MIMICS) model, which can then be slotted into the decomposition module of our global biogeochemical model, the Terrestrial Ecosystem Model (TEM). This work will improve the integration physical protection and C complexity into climate models, and scale measured biological, chemical and physical parameters to improve predictions of global C cycle feedbacks in a warmer world.

***Carbo-Nutrient Economy of the Rhizosphere: Improving Biogeochemical Prediction and Scaling Feedbacks from Ecosystem to Regional Scales***

- **Principle Investigator:** Joshua Fisher (JGI, University of California)
- **Collaborators:** Richard Phillips (Indiana University); Edward Brzostek (West Virginia University); Tom Evans (Indiana University)
- **Total Award:** \$599,835 over 3 years
- **Award Number:** DE-SC0016188

We as society continue to increase CO<sub>2</sub> in the atmosphere, which traps energy, leading to a wide range of changes in Earth processes, such as water cycling and ecosystem function. It is these ecosystems, however, that are the primary

mechanism by which the Earth can re-soak up that CO<sub>2</sub> out of the atmosphere. Nonetheless, as most gardeners and farmers know very well, the ability of plants to grow—and take up CO<sub>2</sub>—is typically limited by the amount of nutrients (i.e., nitrogen, phosphorus) available to plants.

As one walks through a forest, unseen to us is a vast underground network of fungi that operates in a complex economy, whereby fungi scavenge for nutrients and trade them to trees in exchange for carbon sugars. This helps the plants alleviate some of that nutrient deficiency; but, at the same time, the plants lose carbon that they could have otherwise used for growth of leaves, wood, and roots. The amount of carbon required to “pay” the fungi for a given amount of nitrogen or phosphorus varies from fungi to fungi. Hence, this carbon-nutrient economy is complex with large implications on how ecosystems may or may not be able to soak up CO<sub>2</sub> now and into the future.

Our future projections of the state of the Earth derive from Earth System Models, which formulate Earth processes into myriad mathematical equations run on powerful supercomputers. If processes are missing or the equations are wrong, then this may lead to error in the projections. Currently, these models have not yet included the plant-fungi nutrient economy, primarily because we have not had the key measurements upon which to construct the mathematical equations, until now. Our science team has developed cutting-edge techniques to measure the carbon and nutrient flows between the soil and plants, mediated through plants and fungi, thus enabling the advancement of the modeling of the Earth System. Our project will add this nutrient economy to the models, resulting in significant advances of Earth System Models and understanding of how plants, fungi, and their carbon-nutrients feedback to one another, and to the Earth System as a whole

***Wood Decomposition and Mineral Soil C: Using the d13C Signature in FACE Wood to Measure the Contribution of Dead Wood to Mineral Soil C Pools***

- **Principle Investigator:** Carl Trettin (US Forest Service)

- **Collaborators:** Debbie Page-Dumroese (US Forest Service); Daniel Linder (US Forest Service); Brian Forschler (University of Georgia); Andrew Burton (Michigan Technological University); Martin Jurgensen (Michigan Technological University); Zhaohua Dai (Michigan Technological University); Jonathan Schilling (University of Minnesota)
- **Total Award:** \$597,909 over 3 years
- **Award Number:** DE-SC0016235

The amount of carbon stored in terrestrial ecosystems is an important factor in determining productivity and resilience to disturbance, management and changing climatic conditions. Generally, the soil contains much more carbon (C) than the vegetation. The soil C is stored in association with mineral soil materials, affecting nutrient cycles and water holding capacity. Understanding the sources of the soil C and the processes that result in its formation is fundamental to the sustainability of terrestrial ecosystems. Dead wood is a significant terrestrial carbon pool, comprising 10- 20% of the forest biomass in the U.S. A major uncertainty in the terrestrial C cycle is the transfer of C from dead wood into the atmosphere as CO<sub>2</sub> versus to underlying mineral soil C pool. Documenting the fate of wood C during the decomposition process is difficult because (1) wood decomposition is inherently slow, and (2) C from decomposing wood often cannot be differentiated within the soil matrix. While wood-decay fungi and invertebrates, especially termites, are understood to be the principal agents mediating wood decay, little is known about their ecology or their interactions, nor the process and pathways affecting the transfer of C from wood into the soil.

This study uses an established decomposition experiment with wood grown in elevated CO<sub>2</sub> in the US Dept. of Energy free-air carbon dioxide enrichment (FACE) experiment. By using the unique δ<sup>13</sup>C signature in three species of wood from two FACE sites, we will measure the amount of wood C incorporated into soil organic matter pools, and determine factors regulating wood decomposition processes within nine major forest – bioclimatic zones within the continental U.S. The study objectives are: (1) Determine the influence of wood biochemistry, microbial process, soil properties, and climatic factors on wood decomposition and

incorporation of wood C into mineral soil C pools; (2) Determine the incidence of termite foraging, interaction between termite and fungal community activity and effects on the rate of wood decomposition and incorporation of wood C into mineral soil C pools; (3) Develop a module within the biogeochemical model Forest DNDC to improve estimates of log decomposition and wood C movement into the mineral soil.

This study will be conducted on the FACE Wood Decomposition Experiment (FWDE), where FACE logs were placed in 2011 on nine experimental forests, on representative soil types within different bioclimatic zones across the U.S. An established field-scale termite exclusion experiment provides unique capabilities to assess interaction among microbial communities and subterranean termites. Recent assays from the FWDE affirm that the δ<sup>13</sup>C signature of the FACE wood can be traced into the mineral soil. We will build on these preliminary findings to establish what, biologically, is mediating the amounts of C we are tracing in soil, with specific interest in dominant fungal rot types and the role of termites. Subsequently, we will update Forest DNDC, a model that can be used to simulate the forest carbon cycle at multiple scales under current and future climate conditions and management scenarios. This study should be able to make major advances in understanding the fate of C bound in deadwood, and in improving tools that will help assess the effects of climate change and management regimes.

#### ***Arctic Shrub Expansion, Plant Functional Trait Variation, and Effects on Belowground Carbon Cycling***

- **Principle Investigator:** Jennifer Fraterrigo (University of Illinois)
- **Collaborators:** Feng Sheng Hu (University of Illinois); Josh Peschel (University of Illinois); Ken Tape (University of Alaska); Eugenie Euskirchen (University of Alaska)
- **Total Award:** \$598,410 over 3 years
- **Award Number:** DE-SC0016219

Terrestrial ecosystems are undergoing dramatic changes in response to climate warming, and these changes are expected to feedback to the atmosphere, potentially altering the trajectory of

future climate change. Feedbacks from Arctic ecosystems are a major concern because the Arctic is projected to warm significantly in the 21<sup>st</sup> century and because >50% of global belowground organic carbon is stored in permafrost and overlying soils. Warming-driven release of this carbon could drastically increase atmospheric greenhouse gas concentrations and accelerate climate warming. Plant communities are also responding to warming, as evidenced by the widely documented increase in woody-shrub growth and “greening” across much of the Arctic tundra biome. This vegetation shift may offset or amplify warming by altering carbon cycling. The direction and magnitude of shrub effects remain highly uncertain, however, due to limited understanding of the consequences of shrub expansion for belowground carbon cycling and simplification of these relationships in models. The major shrubs expanding in the Arctic (*Betula*, *Salix*, and *Alnus*) vary widely with respect to aboveground and belowground traits (e.g., tissue production and chemistry, rooting depth, microbial symbionts), and may also exhibit substantial intraspecific variation in these traits in response to environmental conditions. Such variation is likely to have profound implications for soil carbon cycling.

The proposed research will investigate how plant functional traits respond to environmental conditions and affect belowground carbon cycling. We will test the following hypotheses: (1) Aboveground and belowground plant functional traits are determined primarily by air temperature, but edaphic conditions control trait response within a given air temperature range; (2) The response of soil organic carbon cycling to shrub expansion depends on plant functional traits, particularly root traits and microbial symbionts; and (3) Regardless of the dominant species, shrub expansion will interact with physico-chemical processes to increase the pool size of stable soil organic carbon in the mineral soil. To test these hypotheses, we will quantify relationships among aboveground and belowground plant functional traits and carbon cycling along topo-edaphic gradients nested within a temperature gradient in the Alaskan tundra. Using this temperature-by-topography design, we will characterize aboveground and belowground plant functional trait variation for individual shrub species, determine how aboveground and belowground traits co-vary,

and evaluate relationships between plant functional traits and carbon stocks and fluxes. We will also use Bayesian data-model fusion methods to improve the parameterization and formulation of the Terrestrial Ecosystem Model, which is widely used in Arctic carbon studies. We will then perform simulation experiments to evaluate how differences in plant functional traits affect carbon dynamics over time, and explore approaches to accounting for this variability in models. We will hold a workshop with the modeling community to disseminate our results, refine recommendations for model improvement, and initiate collaborations to implement these recommendations in existing models of tundra carbon dynamics at ecosystem to Earth system scales.

The proposed research directly supports the DOE near-term priorities by providing mechanistic insights into the role of subsurface processes in the terrestrial carbon cycle in a region that is inadequately represented in Earth system models. Current models reduce the complexity of Arctic vegetation to a small number of plant functional types (PFTs). This approach implicitly assumes that each PFT represents the average ecological function of its constituent species, thus ignoring the effects of trait variation on carbon cycling and potentially leading to large uncertainty in the sign and magnitude of ecosystem feedbacks to climate. The proposed research directly confronts this issue by investigating variation of plant functional traits across broad gradients of climatic and topo-edaphic conditions and by elucidating the linkages of such variation with carbon cycling. This knowledge is necessary for developing an alternative modeling approach that allows the traits of PFTs to vary as a function of environmental conditions, thereby enhancing the capacity of simulation models to offer insights into ecosystem carbon dynamics associated with novel plant communities in a rapidly changing Arctic.

### **Subsurface Biogeochemistry Research (SBR)**

#### ***A Vegetative Facies-Based Multiscale Approach to Modeling Nutrient Transport in the Columbia River Basin***

- **Principle Investigator:** Ilenia Battiato (San Diego State University)
- **Collaborators:** Felipe de Barros (University of Southern California)
- **Total Award:** \$150,000 over 1 year
- **Award Number:** DE-SC0016484

The impact of submerged vegetation on nutrient and contaminant distributions has been generally overlooked in recent multiscale modeling efforts. Yet, vegetation is the regulatory layer between many hydrological and ecological functions and plays a pivotal role in regulating fluxes between the surface waters and groundwater. One common challenge in modeling transport in vegetated rivers is the lack of predictive models linking vegetation type and topology with effective transport properties of the vegetative layer itself and its dynamic linkages to its surroundings, while accounting for the multiscale nature of a vegetated system.

The goal of this exploratory research is to develop the foundations of a multiscale framework to understand and predict the impact of the morphological characteristics of vegetation on transport of nutrients and contaminants in vegetated rivers over a multiplicity of scales, and to provide computational tools for robust uncertainty quantifications in multiscale simulations. This will be achieved through a combination of analytical and computational tools, while assimilating (e.g. LiDAR) data of vegetation coverage and type. Under the hypothesis that vegetative layers can be treated as porous media, topological features of the vegetation will be linked to effective porous medium properties such as porosity, permeability and dispersion tensor through a physically-based multiscale numerical analysis. The models developed will be tested against available data collected in vegetated channels across the United States, including the Columbia River Basin. A classification of vegetative-facies will be proposed based on the primary function that a specific type of vegetation executes in the system. The methods and algorithms developed in the course of the proposed activity will lay a solid foundation for improved quantitative understanding of the role of vegetation in regulating nutrient and energy fluxes between rivers and the subsurface interaction zone (SIZ) at the basin scale.

***A Last Line of Defense: Understanding Unique Coupled Abiotic/Biotic Processes at Upwelling Groundwater Interfaces***

- **Principle Investigator:** Martin Briggs (US Geological Survey)
- **Collaborators:** Frederick D. Day-Lewis (US Geological Survey), Lee Slater (Rutgers), Kenneth Williams (Lawrence Berkeley National Laboratory)
- **Total Award:** \$539,295 over 3 years
- **Award Number:** DE-SC0016412

Groundwater seeping from sediments into lakes, wetlands, and rivers generates approximately 70% of total surface water flow in the USA. Fish such as trout and salmon can use groundwater seepage zones for spawning and for refugia to survive warm surface water events in summer. However, this groundwater can carry contamination, and therefore threaten surface water quality. Fortunately, like a fish tank filter, the shallow interface sediments that line surface water bodies can host beneficial bacteria that naturally remove contaminants from groundwater as it strains through tiny pores on the way to the surface. When water that is low in dissolved oxygen reaches the oxygenated surface water, metal oxides (rust) may be deposited in layers 10's of cm thick. These soupy deposits of iron (red) and manganese (black) metals are often observed around wetlands at groundwater seeps. The former can be referred to as "bog iron," and was mined extensively for tools and weapons from ancient to colonial times. These deposits of metal oxides, which are also observed in abundance within mine-impacted watersheds, act as "contaminant sponges" that pull toxic chemicals out of solution. These toxins include arsenic and uranium, which often threaten animal and human health. However, dissolved oxygen levels in surface and shallow groundwaters are highly dynamic, and if oxygen with shallow interface sediments is decreased, metal oxides may dissolve and their contaminants may be released as a toxic pulse.

The hydraulic pressures that affect oxygen exchange, and in turn, drive metal-oxide deposition and dissolution are complicated and currently not well defined. Further, there is emerging evidence that the metal-oxide deposits may act as strong conductors of heat and electricity, which likely affects sediment reaction rates including carbon cycling and the

contaminant sponge-functionality. We plan to extensively study metal oxides in the laboratory and within a mine-impacted watershed in Colorado to: (1) better understand how dissolved carbon and contaminants pass from groundwater to surface water, and (2) capitalize on the ability of natural systems to adsorb and sequester contaminants. This study will result in predictive, processes-based understanding of the paired stream and groundwater conditions that lead to metal-oxide deposition so our water resources can be better managed and used.

***Exploratory Research: Transport and Transformation of Particulate Organic Matter in Permeable Riverbed Sediments***

- **Principle Investigator:** Matthew Ginder-Vogel (University of Wisconsin)
- **Collaborators:** Eric Roden (University of Wisconsin), Steven Loheide (University of Wisconsin)
- **Total Award:** \$126,140 over 1 year
- **Award Number:** DE-SC0016217

The proposed research is designed to build a fundamental, quantified understanding of the deposition, transport and processing of particulate organic matter (POM) into the riverbed within large river ecosystems to address these deficiencies by leveraging knowledge developed as part of the PNNL Science Focus Area (SFA). In particular, we will examine particulate organic matter (POM) deposition, transport, and transformation in simulated, near-shore Columbia River (CR) sediments through a series of column experiments. This research is exploratory in nature and is designed to lay the foundation for future experiments characterizing biogeochemical processes associated with POM accumulation in actual permeable riverbed sediments. The primary goals of this limited set of experiments are to: 1) determine the physiochemical processes controlling the POM accumulation within riverine sediments, and 2) quantify microbial metabolism driven by this accumulation.

Although rivers are often conceptualized as the water column and the bed, by far the greatest biogeochemical activity takes place in the riverbed, either at or just below the surface. This is because the concentration and residence time of organic matter and associated

microorganisms in sediments is typically several orders of magnitude greater than that in the overlying water.

From a hydrological perspective, permeable benthic and hyporheic sediments can be considered as reactive sieves or filters through which flowing water carries particulate and dissolved material. Where the riverbed is permeable, entrained suspended particles and dissolved material can be transported into the bed on strong downwelling flows to be deposited and processed at depth. Thus, the sediments are a focal point for material carried by the river, concentrating both allochthonous and autochthonous organic matter. Organic matter (particulate or dissolved) in the sediment provides electron donors to support an array of respiratory and fermentative reactions, with the former consuming oxygen and, in turn, alternative electron acceptors such as nitrate, Fe(III) oxides, and sulfate once the oxygen is diminished or fully depleted.

The planned research addresses a need to understand whether advectively-transported fine particles penetrate the armor layer and move deeper into the upper-most hyporheic interstices, with a specific focus on determining the extent to which POM can move into the hyporheic zone as a function of the transport properties of the organic particles. Although previous studies have directly examined the uptake and degradation of POM in permeable marine sediments, little to no research has been conducted to specifically quantify POM transport in the context of colloid filtration theory and transport-reaction modeling. This question thus represents a key knowledge gap that this exploratory (and subsequent additional) research will address.

River stage plays a key role in the mixing of groundwater and surface water in the permeable riverbeds of the Columbia River (CR). The water table and associated groundwater gradients within the Hanford Reach of the CR are strongly influenced by river stage (height) fluctuations. As water levels fluctuate, the gradient between the river and groundwater fluctuates. Simulations of water flow direction and magnitude performed by the PNNL SFA indicate that the average flow direction is into the riverbed sediments; however, the flow magnitude varies between ~0.05 and ~0.2 m/h

into the sediment with flow rates of ~0.1 m/h the most prevalent. Depending on river stage, the water flow direction even reverses with flow rates of up to ~0.1 m/h out of the sediment.

The proposed research complements and extends research being performed at a number of SBR-funded PNNL SFA program, which is focused on developing a predictive model of groundwater-surface water interaction and biogeochemical processes within and beyond the Hanford reach of CR. However, POM transport input and degradation within near-surface sediments is not currently a focus of the PNNL SFA.

***Understanding Ecohydrological Controls of Biogeochemical Reactions and Fluxes: Comparison of Two Contrasting Watersheds***

- **Principle Investigator:** Li Li (Pennsylvania State University)
- **Collaborators:** Jason Kaye (Pennsylvania State University), Yuning Shi (Pennsylvania State University), Carl Steefel (Lawrence Berkeley National Laboratory), Kenneth Williams (Lawrence Berkeley National Laboratory)
- **Total Award:** \$180,000 over 1 year
- **Award Number:** DE-SC0016221

We propose to develop predictive understanding of key drivers of metal export at the watershed scale. It is well documented at the laboratory scale that metals form complexes with dissolved organic carbon (DOC). Preliminary data from the Coal Creek, Colorado, have also indicated similar connections – the concentration and discharge relationships of metals such as Cd and Zn mirror those of DOC demonstrating strong flushing (chemodynamic) behavior, in contrast to the chemostatic behavior of geogenic species that are the products of chemical weathering. In other words, in the high elevation Coal Creek watershed, most metal export occurs during the high flow - spring melt period. Here we hypothesize that hydrology-driven soil carbon decomposition releases DOC and drives metal export from Coal Creek. Developing predictive understanding of metal export at the watershed scale however requires an integrated approach to systematically explore the connections among hydrological processes, soil carbon decomposition into DOC, and metal export.

Although extensive studies and model development focusing on distinct aspects of watershed processes have significantly advanced soil biogeochemistry and hydrology sciences, modeling tools that integrate ecohydrological drivers and biogeochemical fluxes are largely lacking. This has limited our ability to understand and to predict water quality of mining-impacted watersheds. The objective of this project is to 1) develop a general purpose bioRT module for soil carbon-mineral-water interactions; integrate the module into DOE-BER suite of codes for a wider user community; 2) apply the model to understand key drivers of metal export from Coal Creek. Such a modeling tool is important not only for Coal Creek, CO, but also for other human-impacted watersheds including those in Appalachian Basin that extends thousands of miles. Human activities including historical mining and current natural gas production have threatened water resources that are important for tens of million people. Predicting capabilities are also essential in understanding the responses of these contaminated watersheds to changing climate.

***Characterization of Groundwater Flow and Associated Geochemical Fluxes in Mineralized and Unmineralized Bedrock in the Upper East River and Adjacent Watersheds, Colorado***

- **Principle Investigator:** Richard Wanty (US Geological Survey)
- **Collaborators:** L. Ball, J. Caine, M. Kass, A. Manning, B. Minsley, P. Verplanck (US Geological Survey)
- **Total Award:** \$599,738 over 3 years
- **Award Number:** DE-SC0016250

This project brings together interdisciplinary strategies for improving the state of knowledge regarding the influence of deep-circulating bedrock groundwater on stream flows and stream-water chemistry in mountain watersheds. This influence may be significant, given that bedrock groundwater discharge can be volumetrically non-trivial and geochemically highly evolved, but in general remains poorly characterized mainly due to a lack of bedrock monitoring wells in high mountain settings. The proposed work will complement the ongoing ecohydrologic Science Focus Area (SFA) project led by the Lawrence Berkeley National

Laboratory (LBNL) being conducted in the upper East River watershed in the Elk Mountains, Colorado.

Like many rivers with alpine headwaters, the East River watershed contains several zones of exposed mineralized and hydrothermally altered bedrock. Surface and groundwater draining these mineralized zones commonly contains high concentrations of metals and other solutes due to the weathering of sulfide minerals, and can contribute substantially to stream chemical loads. Our work will focus on a mineralized area in the upper East River vicinity, and will include installing bedrock monitoring wells to depths of up to 150 m and performing both surface and subsurface geological characterization, geophysical surveys, geochemical sampling, and aquifer testing. These data will be used, along with generalized numerical models, to characterize the bedrock groundwater flow system and mineral weathering processes, identify geologic and climatic controls, and constrain fluxes of water and solutes in discharging bedrock groundwater. Results will be compared to results of a parallel study employing similar methods in unmineralized areas in the upper East River SFA site (performed as part of ongoing SFA project work) to better understand how the post-depositional mineralization affects groundwater flow and associated elemental fluxes. The ultimate aim of the proposed work is to develop a conceptual model of the deep bedrock hydrogeochemical system in both mineralized and unmineralized areas of the upper East River that could provide the foundation for incorporating the deeper subsurface into the numerical reactive transport model being developed for the watershed by LBNL. Our results will enrich the ongoing LBNL studies by providing a more robust understanding of the bedrock groundwater flow system, and will help forecast the effects of perturbations such as climate change.

***Mechanistic and Predictive Understanding of Needle Litter Decay in Semi-Arid Montane Ecosystems Experiencing Unprecedented Vegetation Mortality***

- **Principle Investigator:** Jonathan Sharp (Colorado School of Mines)
- **Collaborators:** Eoin Brodie (Lawrence Berkeley National Laboratory), Kenneth

Williams (Lawrence Berkeley National Laboratory)

- **Total Award:** \$200,000 over 1 year
- **Award Number:** DE-SC0016451

Mountainous regions across the globe are experiencing major forest disturbances associated with a changing and variable climate. These disturbances alter ecosystems with potential effects and feedbacks on interdependent carbon and nitrogen cycling at the terrestrial interface. Recent large-scale insect infestations are of particular concern as they have the potential to switch the Rocky Mountain region from a carbon sink to a source through the defoliation and degradation of millions of acres of evergreen trees. While it is understood that this will lead to cascading effects in both the hydrosphere and atmosphere, current predictive models are not equipped with the information to incorporate these dynamic and comparatively sudden disturbances relating to carbon decay and release. This one-year project focuses on establishing, instrumenting, and deploying a set of experiments designed to understand needle litter decay rates and underlying mechanisms between evergreen needles released from insect-killed trees to that of naturally senesced litter from healthy trees. The proposed work will be conducted within Rocky Mountain Biological Laboratory's (RMBL) East River watershed in southwestern Colorado, whose forests are threatened by changing temperature, altered hydrological and snowmelt patterns, and invasive insect infestation. Needle litter from two members of the Pinaceae family experiencing large-scale insect infestations (spruce and lodgepole pine) will be collected and redeployed. We will experimentally test three tractable parameters that are known to impact litter decay and biogeochemical cycling and are relevant to bark beetle-induced tree mortality: (1) moisture content, (2) temperature by using elevation as a surrogate, and (3) changes to litter compositional chemistry that result from beetle infestation. We will establish a baseline for decay processes while monitoring the migration of soluble and gaseous nitrogen and carbon species. In addition, we will evaluate variables that are associated with the rate of microbial litter decomposition such as metal availability, enzyme activity, and the temporal succession of associated microorganisms. The studied processes are expected to improve formulation and parameterization of reactive

transport models being developed by DOE National Labs. This approach can help unravel the intertwined response of carbon and nitrogen cycling, microbial processes, and the impacts moisture conditions and temperature have on litter decay feedbacks in a changing climate.

### ***Multi-Scale Modeling Framework for Mercury Biogeochemistry***

- **Principle Investigator:** Jeremy Smith (University of Tennessee)
- **Collaborators:** Jerry Parks (Oak Ridge National Laboratory), Guoping Tang (Oak Ridge National Laboratory)
- **Total Award:** \$540,000 over 3 years
- **Award Number:** DE-SC0016478

Mercury (Hg), and most of its compounds, are extremely toxic to wildlife and humans, causing both chronic and acute poisoning. Natural sources of Hg, such as volcanoes, are responsible for approximately half of atmospheric mercury emissions, with the other half coming from human activities, such as coal-fired power plants. The Oak Ridge Reservation is a site of particular Hg contamination, due to past weapons production activities. Efficient remediation of contaminated sites and prevention of additional contamination requires a predictive understanding of Hg biogeochemical transport and transformation in surface and subsurface environments. The planned research aims to construct a multiscale modeling framework that connects the molecular scale to local (mesoscale), reach and watershed scale models.

The ORNL Mercury Scientific Focus Area (SFA) is presently establishing reach- and watershed-scale modeling capabilities for the East Fork Poplar Creek (EFPC). While it is generally recognized that linking atomistic knowledge to macroscopic scales has considerable potential for improving overall model accuracy, deficiencies in our understanding of basic processes and the lack of development of molecular scale modeling methods has hindered the generation of reliable data and thus the integration of these data across scales to obtain a model of Hg cycling.

The University of Tennessee has recently established a molecular-scale, quantum chemical computational methodology that has

been demonstrated to calculate the structures, rates and binding constants of Hg complexes with organic and inorganic species with chemical accuracy. There is a need to link atomistic and mesoscale modeling to impact field-scale studies and improve the accuracy with which processes that control Hg fate can be modeled.

Research within this project will involve computing the mechanisms, kinetics and thermodynamics of a comprehensive list of Hg chemical processes critical to EFPC. The results of the molecular-scale modeling will be combined with information from existing thermodynamic databases and used as input for local-scale thermodynamic speciation and reactive flow modeling. The computer simulations will make use of DOE supercomputers.

Expected outcomes include mesoscale models that incorporate new atomistic process understanding. The meso-scale modeling will focus on integrated local-scale model systems containing ions, natural organic matter and microbes, and will include the modeling of critical geochemical gradients. The results will be tested by comparison with key speciation and kinetic experiments existing in the literature and being performed within the ORNL SFA program. When integrated with the work being performed in the SFA, the present work will establish a generally-available modeling framework for deploying knowledge gained from molecular-scale Hg models up to the field scale. The established computational framework will be in the future generalizable to other metals, and will be able to be continuously iterated with experiment over all scales to improve modeling accuracy.

### ***Experimental and Modeling Investigation of the Impact of Atmospherically Deposited Phosphorus on Terrestrial Soil Nutrient and Carbon Cycling, and Ecosystem Productive***

- **Principle Investigator:** Peggy O'Day (University of California, Merced)
- **Collaborators:** Stephen Hart (University of California, Merced), Asmert Berhe (University of California, Merced), Marilyn Fogel (University of California, Merced); Harry Beller (Lawrence Berkeley National Laboratory), Nancy Washton (Environmental Molecular Sciences Laboratory)

- **Total Award:** \$200,000 over 1 year
- **Award Number:** DE-SC0016479

An accepted paradigm of terrestrial ecosystems in temperate climates is that nitrogen (N) rather than phosphorus (P) is the dominant limiting nutrient of net primary productivity. Recent studies, however, conclude that anthropogenic releases of N have overwhelmed the N cycle, such that the bioavailability of P rather than N may now control productivity and thus carbon sequestration in many ecosystems, particularly those with low soil P. The importance of atmospheric deposition of P from both natural and anthropogenic sources has been recognized in global biogeochemical cycles, but few studies have directly documented the species of inorganic or organic airborne P deposited to ecosystems, or their bioavailability, fate after deposition, or processing pathways by microorganisms. In general, the relative importance of atmospheric P particulate deposition to local ecosystem productivity has not been examined at the level of detail needed, or with sufficient quantification, for biogeochemical model parameterization. We propose to collect exploratory data that will test the hypothesis that the amount and the chemical speciation of P from atmospheric particle deposition can have a significant impact on net ecosystem productivity in P-limited, N-replete terrestrial environments.

In this exploratory project, we aim to establish the chemical speciation of P in airborne particulate matter deposited at two mountain watershed sites, and evaluate the potential for reactivity and biogeochemical cycling of air-deposited P compared with resident soil P. Air and soil samples will be compared from two sites: one along a well-established altitudinal transect in the Southern Sierra Critical Zone Observatory (SSCZO), and one in the East River Watershed in Upper Colorado River Basin (in collaboration with Lawrence Berkeley National Laboratory (LBNL)). A combination of spectroscopic methods (P XAS, solid-state <sup>31</sup>P NMR, FTIR), source characterization using stable isotopes ( $\delta^{18}\text{O}$  in  $\text{PO}_4$ ), and selective chemical extractions will be used to determine labile or recalcitrant P species, and to evaluate sources and changes in P speciation with deposition to soil. Pilot experiments using field soils in controlled laboratory microcosms with the addition of isotopically labeled, model

inorganic or organic P compounds will examine the feasibility of tracking microbially catalyzed P transformations. We will collaborate with scientists at LBNL for sample collection at the East River site, and draw on their unique expertise for molecular environmental microbiology characterization. Data will be synthesized and simulated in a preliminary reactive transport biogeochemical model. This project will take advantage of DOE-supported facilities (the Environmental Molecular Sciences Laboratory at Pacific Northwest National Laboratory for NMR studies; the Stanford Synchrotron Radiation Lightsource for XAS). These studies will establish whether the chemical forms of P from atmospheric particle deposition have significant reactivity for incorporation into soil biogeochemical cycles, and thus may have a potentially large and disproportionate impact on net ecosystem productivity in P-limited terrestrial ecosystems.

#### ***Seasonal Controls on Dynamic Hyporheic Zone Redox Biogeochemistry***

- **Principle Investigator:** Michael Wilkins (Ohio State University)
- **Collaborators:** Audrey Sawyer (Ohio State University), Kenneth Williams (Lawrence Berkeley National Laboratory)
- **Total Award:** \$182,424 over 1 year
- **Award Number:** DE-SC0016488

Hyporheic zones (HZs) are regions of groundwater-surface water mixing that play an outsized role in biogeochemical cycling and chemical export, especially in upland watersheds that are recognized as net exporters of organic carbon, metals, and other nutrients. In semi-arid western U.S. watersheds, snowmelt-linked patterns of river discharge drive seasonal fluctuations in redox conditions across the HZ; under high discharge conditions (e.g., during snowmelt), oxic river water penetrates deeper into riverbed sediments, while under low discharge (base flow) conditions, the upward flow of reducing anoxic groundwater limits the depth of hyporheic mixing. However, the impacts of these redox perturbations on the functioning of microbial assemblages and associated biogeochemical processes in the HZ are currently unknown. This project seeks to quantify and model (1) biogeochemical responses to seasonal snowmelt-driven expansion and contraction of HZs and (2)

implications for solute fate in high-altitude temperate rivers.

The proposed one-year effort will leverage pre-existing metadata and excellent experimental infrastructure in the East River watershed as part of a study in western Colorado led by the Lawrence Berkeley National Laboratory (LBNL) Scientific Focus Area (SFA). The East River site represents a pristine watershed, where snowmelt drives a period of high discharge in early summer followed by a period of lower discharge during fall and winter. Arrays of in situ, depth-resolved redox and temperature probes will be installed across a series of meanders in the East River to monitor real-time changes across the HZ. These data will be complemented by sampling campaigns at three time points in the hydrograph (peak and intermediate discharge, and base flow) to obtain HZ sediments and pore fluids. These materials will be used for a series of high-resolution analyses to measure changes in carbon pools and aqueous metals over seasonal time points. Coupled to these geochemical observations, assembly-based metagenomic and transcriptomic tools will resolve changes in microbial functional potential and activity across time and space, and will allow us to elucidate seasonal effects on the linkages between HZ hydrology, microbiology, and chemistry. Additional activity measurements using radiotracer analyses will further help to resolve these linkages. Finally, these diverse datasets will be used to develop 1-D coupled reactive transport-biogeochemical models of HZ processes. Model results will be used to quantify seasonal changes in chemical fluxes across the sediment-water interface, reaction rates per unit area of streambed, and forcings between hydrodynamics and biogeochemical dynamics. Specifically, we will be able to quantify transport and reaction rates during field campaigns and also infer potential changes across the year when we lack observations. Additionally, sensitivity studies will also be performed to explore biogeochemical responses to future annual hydrograph scenarios. We will vary both river discharge and vertical seepage rates to mimic changes in snowmelt timing, duration, and base flow contribution.

Results from this study will be critical for assessing (1) hyporheic control over export of metals, carbon, and other nutrients from upland

watersheds, and (2) how HZs in such watersheds may respond to future changes in river discharge under a warming climate and changes in the hydrologic behavior of snowmelt dominated systems. Changes in climate patterns in the coming decades are projected to impact hydrology across much of the United States, with potential decreases in snowpack and earlier snowmelt forecast for in the intermountain West, which likely will greatly alter river discharge behavior and drive changes in riverine ecosystems. We will actively integrate with LBNL SFA research efforts, with the studies proposed here offering valuable complementary information on the mechanistic behavior of HZ processes. Additional collaborations will be sought with the IDEAS Use Case 1 team.

***Use of Stable Mercury Isotopes to Assess Mercury and Methylmercury Transformation and Transport across Critical Interfaces from the Molecular to the Watershed Scale***

- **Principle Investigator:** Jason Demers (University of Michigan)
- **Collaborators:** Joel Blum (University of Michigan), Scott Brooks (Oak Ridge National Laboratory)
- **Total Award:** \$539,992 over 3 years
- **Award Number:** DE-SC0016489

The over-arching goal of this effort is to use natural mercury (Hg) stable isotope signatures, imparted by molecular-scale reactions, to gain a more comprehensive quantitative and mechanistic understanding of the processes that supply dissolved Hg to surface water and thus drive observations of watershed-scale mercury fluxes in the East Fork Poplar Creek (EFPC) ecosystem near Oak Ridge, Tennessee. We also aim to elucidate the sources of methylmercury and the balance of reactions that govern its production and fate in this Hg-contaminated stream ecosystem. To achieve these goals, we will integrate mercury isotopic analysis with ongoing efforts of the field-based SBR SFA at ORNL to provide a synergistic multiple-lines-of-evidence approach for assessment of Hg transformation and transport across critical interfaces within the EFPC ecosystem.

Much has been learned about Hg cycling in lotic systems, and East Fork Poplar Creek in particular, through decades of previous

research. Nevertheless, some of the most fundamental questions regarding the source(s) of bioavailable Hg and its transformation to toxic methylmercury (MeHg) remain unanswered. These fundamental questions include: 1) the source(s) and biogeochemical processes that lead to the input of dissolved Hg to EFPC stream water, and 2) the source(s) and biogeochemical processes that control the production and fate of bioaccumulative MeHg in the EFPC ecosystem. To address these fundamental questions, this project aims to couple laboratory experiments and field observations, and use natural abundance Hg stable isotope techniques to identify the processes responsible for generating bioavailable dissolved Hg from relatively recalcitrant legacy sources of Hg within critical subsurface zones (e.g., hyporheic zone, riparian wetlands, groundwater, and streambed periphyton). Moreover, we propose to use the isotopic signature of this bioavailable dissolved Hg to track its mobilization across critical interfaces in order to directly link diffuse subsurface sources of dissolved Hg with increases in surface water dissolved Hg flux measured at the watershed scale. Furthermore, we will directly determine the isotopic composition of MeHg within these same critical subsurface zones. Using natural Hg isotope signatures, we will assess the direct linkage between the dissolved Hg supply and the MeHg generated within and released across these critical interfaces, and we will evaluate the in situ balance of methylation and demethylation reactions that lead to net production of MeHg in EFPC.

The Department of Energy (DOE) oversees many large environmental remediation operations, and the biogeochemical transformation of mercury (and other contaminants) has been identified as a key contaminant of concern. In order to manage Hg contaminated sites and make informed decisions about Hg remediation strategies, additional tools are needed to trace the sources, pathways, and bioavailability of Hg. Mercury isotopes have been demonstrated to be an important new tool in Hg research and have provided important new insights into mercury biogeochemistry in EFPC and other lotic ecosystems. We propose to further develop and apply this rapidly evolving tool to trace the location of inorganic Hg methylation and the

pathways for the transport and transformation of mercury within the EFPC ecosystem. By identifying the dominant reaction pathways and transport processes underlying watershed scale phenomena, this approach will provide a logical guide for the development of process-rich mechanistic models that will help predict the outcome of remediation efforts, and anticipate the effects of global environmental change on the hydrobiogeochemical cycling of Hg in stream ecosystems. Moreover, such insight will aid in the development of an approach that integrates stable Hg isotope techniques with more traditional watershed-scale approaches, thus serving as a model for future study of other point-source and non-point-source Hg-contaminated watersheds.

#### ***Diagnosing Dominant Controls on Carbon Exchanges in High Altitude, Western U.S. Headwaters***

- **Principle Investigator:** Reed Maxwell (Colorado School of Mines)
- **Collaborators:** David Gochis (National Center for Atmospheric Research), Lindsay Bearup (Lawrence Berkeley National Laboratory)
- **Total Award:** \$170,000 over 1 year
- **Award Number:** DE-SC0016491

Mountain ecosystems are poorly resolved and represented in Earth System Models. However, these regions contribute much of the water and carbon regionally. High elevation ecosystems are dynamic, making quantifying their behavior a challenge. We need to represent the processes governing carbon and water fluxes and storage to understand and predict the impacts of a changing climate on carbon and water fluxes in these critical ecosystems. We currently lack this capability. Observing soil saturation and groundwater levels and their exchange with the lower atmosphere in high-elevation ecosystems is a challenge and these quantities impact subsurface biological activity and greenhouse gas production. This proposed work would close gaps in both the measurement and modeling of these key ecosystems to improve our understanding of their function and their representation in Earth System Models. This project connects several currently disconnected activities to measure and model high-elevation carbon and water interactions. This project will bridge scales to unify these

observations and models to move toward a new regional observatory to quantify these interactions and implement an enhanced, multi-scale data assimilation and modeling capability with links to global earth simulation models. This project will advance the understanding of subsurface storages of water and carbon in addition to understanding ecosystem exchanges. It will also provide atmospheric flow measurements and simulation, to better understand the relationship with changing daily and seasonal carbon dioxide fluxes.

***Metabolic Constraints of Organic Matter Mineralization and Metal Cycling During Flood Plain Evolution***

- **Principle Investigator:** Scott Fendorf (Stanford University)
- **Collaborators:** Marco Keiluweit (University of Massachusetts), Markus Kleber (Oregon State University)
- **Total Award:** \$593,581 over 3 years
- **Award Number:** DE-SC0016544

Floodplains are poorly understood and dynamic components of the global carbon cycle that not are well represented in Earth system models. Further, they have a dominant influence on the cycling of important metals, such as uranium, within critical transport conduits between surface waters and groundwater. The physical characteristics of floodplains make the hydrology and associated coupled biology and geochemistry particularly responsive to ongoing and impending changes in climate, river management, and land development. The limited change in slope coupled with variations in sediment deposits leads to change in particle size distribution (sand, silt, and clay) and particulate organic matter levels results in dramatically different microbial metabolisms across small spatial scales. Overbank sedimentation and infilling of abandoned oxbows (old river channels) within floodplains represents an important sink for carbon on a global scale, and they have a dominant influence on the fate of metals within the floodplains.

We are investigating how metabolic rates of carbon oxidation to carbon dioxide and change in iron and uranium chemistry are controlled

under oxygen limited conditions of the subsurface. We posit that the thermodynamic viability of reactions coupling the oxidation of specific carbon compounds with the reduction of iron(III) and uranium(VI) has a dominant constraint on their fate. Our proposed research specifically focuses on the role of iron in controlling organic matter oxidation both through complexation and thermodynamic restrictions in metabolic energy yield. We focus on iron both because of its quantitative importance within soils/sediments, for anaerobic microbial metabolism and for its (nearly) universal control on binding of metal contaminants such as uranium.

The overarching goals of our proposed research are to decipher the coevolution of organic carbon and iron chemistry within floodplains, and its resulting determinant of carbon oxidation rates and metal contaminant fate and transport. Our specific objectives to meet the goal of our proposed research are to: (1) Define how organic matter evolves within floodplains, (2) Establish the roles of differing iron(III) minerals in limiting anaerobic microbial respiration, (3) Determine the combined influences of organic matter—iron interactions on rates of carbon oxidation or methane production within the varying redox/hydrologic regimes, and (4) Determine how the combined evolution of organic carbon and iron mineralogy within redox regimes impacts uranium fate and transport within floodplains.

We will conduct field and laboratory measurements and experiments that will direct modeling efforts of carbon and metal fate. We will utilize the East River and tributary Slate River floodplains in Colorado, along with the Little Wind River (Riverton), WY floodplain, a uranium legacy management area. Using laboratory experiments composed of field isolated materials in combination with field measurements, we will quantitatively determine the electron acceptors active in microbial respiration across variable and permanently saturated zones and across different sediment ages (using the space-time link of depositional systems). Finally, we will integrate our field and laboratory measurements/experiments into carbon dynamics for Earth System Models and reactive transport codes for contaminant fate and transport.

Further information on TES objectives along with a listing of past and current funding opportunities discussed in this document, is available at <http://tes.science.energy.gov/>.

Further information on SBR objectives along with a listing of past and current funding opportunities discussed in this document, is available at <http://science.energy.gov/ber/research/cesd/subsurface-biogeochemical-research/>

**Contact:**

Dr. Daniel Stover  
U.S. Department of Energy  
Office of Biological and Environmental Research  
Climate and Environmental Science Division  
Terrestrial Ecosystem Science Program  
Phone: 301-903-0289  
Email: [Daniel.Stover@science.doe.gov](mailto:Daniel.Stover@science.doe.gov)

Dr. Jared DeForest  
U.S. Department of Energy  
Office of Biological and Environmental Research  
Climate and Environmental Science Division  
Terrestrial Ecosystem Science Program  
Phone: 301-903-1678  
Email: [Jared.DeForest@science.doe.gov](mailto:Jared.DeForest@science.doe.gov)

Dr. David Lesmes  
U.S. Department of Energy  
Office of Biological and Environmental Research  
Climate and Environmental Science Division  
Subsurface Biogeochemical Research Program  
Phone: 301-903-2977  
Email: [David.Lesmes@science.doe.gov](mailto:David.Lesmes@science.doe.gov)

Mr. Paul Bayer  
U.S. Department of Energy  
Office of Biological and Environmental Research  
Climate and Environmental Science Division  
Subsurface Biogeochemical Research Program  
Phone: 301-903-5324  
Email: [Paul.Bayer@science.doe.gov](mailto:Paul.Bayer@science.doe.gov)

Dr. Roland Hirsch  
U.S. Department of Energy  
Office of Biological and Environmental Research  
Climate and Environmental Science Division  
Subsurface Biogeochemical Research Program  
Phone: 301-903-9009  
Email: [Roland.Hirsch@science.doe.gov](mailto:Roland.Hirsch@science.doe.gov)

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