



# **Subsurface Biogeochemical Research**

## **University Awards**

**Poster #183**

**A Vegetative Facies-Based Multiscale Approach to Modeling Nutrient Transport**

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The impact of submerged vegetation on nutrients and contaminants distribution in the Columbia Plateau region 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 fluvial systems. 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 (i.e. groundwater and surface waters). Specifically, existing models provide only limited understanding of the mechanistic connection between vegetation topology and its function. We address this challenge by modeling the vegetated layer as a porous medium. Such an underlying hypothesis allows us (i) to establish a mechanistic relationship between vegetation structure (e.g. LAI, height, density) and function (permeability, effective dispersion and reaction rates of the canopy layer), and (ii) to construct a framework, and corresponding mathematical machinery, to model the impact of vegetation on nutrient cycling.

## Poster #162

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

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Groundwater seeping from sediments into lakes, wetlands, and rivers generates approximately 70% of total surface water flow in the USA. However, groundwater can carry excess nutrients and other contaminants, and therefore threaten surface water quality. Fortunately, the shallow interface sediments that line surface water bodies can host beneficial bacteria that naturally remove contaminants from groundwater as it strains through pores on the way to the surface. When water that is low in dissolved oxygen reaches the oxygenated surface water, metal (typically Fe, Mn) oxides 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, or can coat solid grains in faster flowing systems such as the East River, CO. These deposits of metal oxides, which are also observed in abundance within mine-impacted watersheds, act as "contaminant sponges" that sorb toxic compounds. These toxins include arsenic and uranium, which 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 sequestration. 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.

**Poster #193**

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

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Historical and ongoing releases of mercury (Hg) have resulted in a legacy of Hg contamination in streambed sediment, stream banks, and floodplain soils downstream of the Y-12 National Security Complex (Y12), along the flow path of East Fork Poplar Creek (EFPC) near Oak Ridge, Tennessee. Much of the Hg associated with streambed sediments, stream banks, and floodplain soils resides in relatively insoluble fractions, and has thus been considered to have little impact on dissolved total Hg (THg) concentrations. However, recent studies comparing hydrologic discharge and THg flux from Y12 and the Lower EFPC suggest that additional dissolved Hg from either the hyporheic zone, riparian wetlands, or groundwater discharge may variably contribute as much as 16-80% of downstream dissolved Hg loads during base flow conditions. Thus, one of the over-arching goals of this project is to use natural 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 drive observations of watershed-scale mercury fluxes. To achieve this goal, we are coupling the Hg isotopic composition of dissolved Hg in stream water and in critical subsurface ecosystem compartments (i.e., hyporheic zone, riparian wetlands, and groundwater) with hydrologic flux measurements in four gauged reaches of EFPC. This will enable us to establish an isotope mass balance that assesses the relative importance of dissolved Hg contributed to the stream across these critical interfaces.

During the first six months of this project we have: (1) initiated monthly base flow surface water sampling to characterize changes in the concentration and isotopic composition of dissolved Hg in each of four gauged reaches of the EFPC; (2) installed infrastructure (semi-permanent piezometers) for sampling hyporheic pore water; and (3) collected the first seasonal sampling of hyporheic pore water and riparian groundwater from five locations along the flow path of the Lower EFPC. Here, we present dissolved Hg concentration and Hg isotopic composition of all surface water, hyporheic pore water, and riparian groundwater samples analyzed to date, and begin to make mass balance assessments regarding legacy inputs of dissolved Hg to the stream water of EFPC.

## Poster #203

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

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Floodplains are poorly understood and dynamic components of the global carbon cycle that are not 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.

An important control on carbon cycling within soils and sediments is constraints on microbial metabolisms induced by the respiratory pathway, and specifically the electron acceptor in respiration, which further serves to control metal fate and transport. Within floodplain soils and sediments, variations in hydrologic state (water saturation) coupled with structured porous media lead to extensive heterogeneity in redox environments and thus metabolic trajectories controlling organic carbon oxidation.

Combining micro-scale laboratory experiments with field-scale observations, we find that oxygen diffusion limitations lead to heterogeneous redox profiles, shifting microbial metabolism to less efficient anaerobic SOC oxidation pathways. In both saturated and unsaturated systems, microsensor measurements in combination with gas flux measurements showed that particle size exerts a strong control on the extent of the anaerobic volume, thereby causing an overall decrease in OM oxidation rates. In model soils and sediments, we determined the distribution of operative microbial metabolisms and their cumulative impact on SOM transformations and overall oxidation rates within anaerobic microsites. Metabolic profiling showed that texture-induced anaerobic microsites reduced carbon oxidation rates by an order of magnitude relative to aerobic rates, with Fe reduction contributing more than 75% of the overall metabolism. Density separations in combination with C 1s NEXAFS spectroscopy and high-resolution FT-ICR-MS showed that texture-induced anaerobic microsites resulted in the preferential preservation of reduced (electron-rich) organic carbon compounds (both dissolved and particulate), a result corroborated by field measurements across multiple sites. Near-edge X-ray absorption spectroscopy similarly indicates a loss of oxidized functional groups within the anaerobic domain.

Collectively, our results suggest that anaerobic zones have prominent controls on organic carbon oxidation in both saturated and unsaturated soil/sediment, thermodynamically stranding reduced carbon compounds. Removing anaerobic metabolic constraints upon a shift in oxygenation will stimulate microbial oxidation of thermodynamically protected carbon.

## Poster #218

### Sensitivity of Transpiration to Subsurface Properties

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The amount of moisture transpired by vegetation is critically tied to the moisture supply accessible to the root zone. In a Mediterranean climate, integrated evapotranspiration (ET) is typically greater in the dry summer when there is an uninterrupted period of high insolation. We present a 1D model to explore the factors that may sustain ET. The model includes a stochastic parameterization of hydraulic conductivity, root water uptake efficiency and hydraulic redistribution by plant roots. Model experiments vary the precipitation, the seasonality of ET demand, and rooting profiles and rooting depths of the vegetation. The results show that the amount of subsurface moisture remaining at the end of the wet winter is determined by the competition between abundant precipitation input, fast infiltration and winter ET demand. In a Mediterranean climate, weathered bedrock provides a not-insignificant reservoir that may sustain ET of deep-rooted (>8m) trees through the dry season. A small negative feedback exists in the root zone, where the depletion of moisture by ET decreases hydraulic conductivity and enhances the retention of moisture. Hence, hydraulic conductivity is impactful in a dry season or a dry year when hydraulic conductivity is reduced, or at a location with less permeable lithology.

## Poster #184

### Transport and Transformation of Particulate Organic Matter in Permeable Riverbed Sediments

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Rivers and other inland water systems are key sites of biogeochemical transformation and storage; they are also distinct ecosystems, geomorphological agents and conduits for material transport across continents to the oceans. Biogeochemical activity in rivers is often conceptualized as occurring predominantly in the water column. However, by far the largest amount of biogeochemical activity takes place within the riverbed, either at or just below the surface. This occurs because the concentration of organic matter (OM) and associated microorganisms is several orders of magnitude higher than the concentration in the water column. Such dynamics have fundamental implications for CO<sub>2</sub> and/or CH<sub>4</sub> production and efflux as well as retention and/or release and transport flux of other nutrients (e.g. N, P) associated with POM decomposition.

Our project is initiating a program of research to examine riverbed Particulate Organic Matter (POM) transport and biogeochemistry in Columbia River (CR) sediments, leveraging knowledge developed as part of the PNNL Science Focus Area (SFA). In particular, we are characterizing POM transport and transformation in simulated, near-shore CR sediments through a series of column experiments. This research is designed to lay the foundation for future experiments and in situ observations characterizing biogeochemical processes associated with POM accumulation and transformation in actual permeable riverbed sediments. The primary goals of this limited set of experiments are to (1) determine the physiochemical processes controlling the POM transport and accumulation within simulated riverine sediments, (2) quantify microbial respiratory metabolism and POM mineralization driven by this accumulation. In addition, we will develop a 1-dimensional transport-reaction model of POM accumulation and metabolism that can be utilized in future experimental studies and could eventually be incorporated into ongoing simulations of hydrological transport and biogeochemical activity in the Hanford 300 Area SIZ.

Current research efforts are focused on quantifying the short-term (< 0.5 day) accumulation of POM in simulated, permeable riverbed sediment. We have examined the transport and accumulation of fresh algal POM in column reactors packed with Hanford sand and fine-grained silt and clay. Parallel experiments are being conducted with latex spheres with an equivalent diameter to the POM. By examining the comparative behavior of the POM and non-living latex spheres we have determined that surface properties of particles and sediment play a critical role in POM transport behavior. The next phase of our research will investigate longer-term (2-4 week) decomposition dynamics of POM in permeable sediments.



## Poster #163

### A Multiscale Approach to Modeling Carbon Cycling Within a High Elevation Watershed

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The rates of soil carbon accumulation, transformation and release to the atmosphere and surface waters remain a key uncertainty in global-scale models. Within the soil environment, residual plant material is transformed into a continuum of organic products of variable accessibility and reactivity. At the watershed scale, averaging over complex soil reaction networks may obscure critical processes; whereas individual soil profiles provide a limited view of the ensemble of pathways that ultimately determines carbon fluxes. To address how collections of spatially and temporally linked reaction networks are manifest at larger scales and the consequences of scale for process-based models, we are studying C fluxes at molecular-level all the way to the watershed-scale within the LBNL SFA East River, CO watershed study site.

To date, we have characterized landscape-scale carbon fluxes within the upper catchment using concentration-discharge relationships and through distributed soil sampling and flux measurements. To understand the biogeochemical and hydrologic dynamics driving these fluxes, we developed two microcatchment study sites at different elevations and life zones (2950 and 3500 m; upper montane and upper subalpine) where we have depth-resolved soil moisture and temperature sensors, soil gas wells and lysimeters paired with measurements of soil surface CO<sub>2</sub> fluxes. Newly developed spectroscopic methods for characterizing molecular-level soil carbon speciation are coupled to field measurements. The depth-resolved CO<sub>2</sub> concentrations suggest that the depth of maximum respiration rates increases throughout the growing season, likely reflecting seasonal drying and the downward movement of optimal soil moisture conditions. An inverse-model of respiration rates suggests two local maxima at shallow (~25 cm) and deep (100-150 cm) depths. This is supported by differences between the observed pCO<sub>2</sub> and model simulations of the microbial dynamics constrained by incubation experiments, indicating that root respiration is vertically offset from the maximum microbial respiration. Collectively, our combined modeling and data collection suggest that vertical movement of water and seasonal shifts in soil moisture distribution are a critical control on subsurface respiration rates that will need to be accounted for in large-scale models.

## Poster #164

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

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An accepted paradigm of terrestrial ecosystems in temperate climates is that nitrogen (N) rather than phosphorus (P) is the dominant limiting nutrient to plant growth. Recent studies, however, suggest that the anthropogenic release of large quantities of oxides of N into the atmosphere through fossil fuel combustion has greatly enhanced N inputs to ecosystems, such that the bioavailability of P rather than N may now control terrestrial productivity. Furthermore, even in relative pristine environments that have low N inputs from the atmosphere but where the soil is derived from low P-bearing geological substrates, P may also regulate ecosystem productivity and the removal of the primary greenhouse gas carbon dioxide from the atmosphere. In this exploratory project, we are using a combination of spectroscopic methods, stable isotopes, and selective chemical extractions to determine labile or recalcitrant P species, and to evaluate sources and changes in P speciation with atmospheric deposition to soil. We are examining initial samples collected in Sept.-Oct. 2016 from two montane 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)). Samples were collected using passive air sampling (static pans) placed at two different elevations at each location. Particulates were washed from the pans, filtered sequentially through 10 and 0.2 micrometer PTFE Teflon filters, and air-dried. X-ray absorption spectroscopy (XAS) at the P K-edge of bulk material on filters showed differences among the two locations and two elevations in both the energy position of the maximum absorbance and in post-maximum edge features. These spectra, in comparison with solid phase reference compounds and phosphate sorbed on mineral surfaces, indicate mixtures of several P species in the dust samples. Further characterization by electron microscopy, solid-state <sup>31</sup>P NMR, and stable isotopes ( $\delta^{18}\text{O}$  in  $\text{PO}_4$ ) is ongoing, as well as chemical analyses and selective extraction. Snow sampling will occur in spring 2017 followed by summer sampling in order to compare differences among particulate material deposited at different times of the year. These studies will help 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.

## Poster #208

### Imaging Radionuclide Transport in Porous Media

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This project is a part of Department of Energy, Experimental Program to Stimulate Competitive Research (EPSCoR) Implementation Grant “*Radionuclide Waste Disposal: Development of Multi-scale Experimental and Modeling Capabilities*”. It includes a combination of lab and field experiments over scales ranging from micrometers to decimeters. A variety of imaging modalities are utilized to image flow and transport processes through pore, column, and lysimeter scales.

1D scans of gamma-ray emitting contaminants have been conducted on lysimeters from the RadFLEX facility at the Savannah River Nationals Laboratory (SRNL). Following weathering of radionuclide contained within a cementitious wastefrom or incorporated into soil for three to four years, the spatial distribution of the radionuclide was quantified with 2.5 mm resolution. These scans showed downward mobility of cobalt-60 and barium-133 when the radionuclides were incorporated directly into the SRNL soil. When radionuclides were incorporated into the cementitious wastefrom positioned in the SRNL soil, cesium-137 exhibited both upward and downward dispersion while the other radionuclides showed no movement. Europium-152 was the only radionuclide of those studied that showed no movement from the original placement within the lysimeter.

Preclinical x-ray computed tomography (CT) technique was used to image macropores and preferential flow paths in the lab columns. Single photon emission computed tomography (SPECT) method, in combination with CT, allowed us to map 3D in-situ contaminant concentration distribution and relate anomalies in transport with the structural features in the porous media. These both methods were used to image the movement, absorption and retention of radionuclides in artificial (such as silica gel, glass beads, filter papers) and natural (SRS soil) materials.

## Poster #209

### Radionuclide Waste Disposal: Development of Multi-scale Experimental and Modeling Capabilities

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This abstract provides a general overview of a DOE Experimental Program to Stimulate Competitive Research (EPSCoR) Implementation grant in South Carolina with supporting funding coming from the BES Heavy Element Chemistry program and the BER Subsurface Biogeochemical Research Program. The objective of this project is to quantitatively describe the influence of coupled physical, chemical, and biological reactions on the migration of radionuclides through porous media. Particular emphasis is placed on determining processes which limit the rates of radionuclide migration including:

1. Impacts of fluid flow, particularly preferential flow, which induce chemical gradients and control the availability of reagents which may influence the mobility of radionuclides.
2. Identification of rate limiting steps of chemical reactions which cause changes in radionuclide mobility as well as the extent of reaction reversibility
3. Characterization of the time and length scales over which non-equilibrium states are maintained based on a competition between chemical reaction rates and physical processes (i.e. flow).

To meet these objectives, we will develop a series of novel, multidimensional tools capable of real time monitoring radionuclide mobility in space and time. This effort will entail development of 2D sensors to monitor chemical states and distribution (i.e. pH, O<sub>2</sub>(aq) concentrations, radionuclide concentrations) in 2D microfluidic cells and macroscale tanks as well as CT and SPECT medical imaging techniques to monitor flow, pore structure, and radionuclide distribution in 4D.

Highlights from several ongoing experimental and modeling studies will be discussed including:

1. Examination of uranyl phosphate dissolution by plant exudates using batch flow through reactors, 2D microfluidic systems, and soil column testing.
2. Development of novel 2D and 3D measurement techniques including x-ray CT and Single Photon Computed Tomography (SPECT) examining Tc-99m transport through porous media. We have evaluated the spatial and temporal resolution limitations of these techniques in an idealized system (i.e. Tc-99m transport through a column packed with glass beads of varying sizes) and also monitored redox driven retention of Tc-99m through soil columns with heterogeneous reducing zones.
3. Quantification of sorption hysteresis and rate limiting steps involved with Cs ion exchange on a sandy loam soil and iodine transformations to organo-iodine species in a wetland sediment. Both studies indicate there is a low concentration but highly reactive component of the soil which controls Cs and I behavior at environmentally relevant concentrations.
4. Field based lysimeter studies of Tc-99 and Np-237 which indicate Tc-99 and Np-237 mobility are highly controlled by oxidation of initially Tc(IV) and Np(IV) sources. The rate and extent of source term oxidation was examined through measurements of Np and Tc in the lysimeter effluents during field deployment as well as leaching, batch sorption, x-ray absorption spectroscopy, and electron microscopy techniques after the lysimeters were retrieved from the field.

## Poster #210

### Natural-Organic Matter and Microbial Controls on Mobilization/Immobilization of I and Pu in Soils and Water Affected by Radionuclide Releases in the USA and Japan

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**Background: a)** <sup>129</sup>I is among the top three risk drivers at DOE Low Level Waste or High Level Waste disposal sites, such as Savannah River Site (SRS). Radioiodine's risk stems largely from its perceived high environmental mobility, large inventory (high fission yield), high toxicity (it is a thyroid seeker), and long half-life (16M years). <sup>129</sup>I exists as multiple species (usually iodide, iodate, and organo-iodine). **b)** The human and environmental risks associated with Pu disposal, remediation, and nuclear accidents scenarios stems mainly from the very long half-lives of several of its isotopes. The SRS, holding one 16 third of the nation's Pu inventory, has a long-term stewardship commitment to investigation of Pu behavior in the environment.

**Methods: a)** Six different genera of Mn(II)-oxidizing bacteria were isolated from SRS soils, and examined for the ability to oxidize iodide directly through enzymatic catalysis, or indirectly through formation of reactive oxygen species (ROS) and/or biogenic manganese oxides. **b)** Humic substances (HAs) from different types of soils in various global regions, were re-suspended with groundwater at a far-field Pu concentration ( $10^{-14}$  M) to examine the influence of natural organic matter (NOM) on Pu partitioning during soil erosion events.

**Results:** Both extracellular enzymes and ROS play a role in microbial Mn(II)-oxidation. Iodide oxidation was not observed in cultures of the most active Mn-oxidizing bacteria. While substantial amounts of Mn(III/IV) oxides were only generated in cultures  $\geq$  pH 6, iodide oxidation was only observed in the presence of Mn(III/IV) oxides when the pH was  $\leq$  5. Iodide oxidation was promoted to a greater extent by synthetic Mn(IV)O<sub>2</sub> than biogenic Mn(III/IV) oxides under these low pH conditions ( $\leq$  pH 5). Thus, the influence of biogenic manganese oxides on iodide oxidation and immobilization is primarily limited to low pH environments.

**b)** Under acidic condition (pH~5.5 as the global averaged soil pH),  $29 \pm 24\%$  of organic matter was released from the HAs, carrying  $76 \pm 13\%$  of total added Pu into mobile colloidal phase. Both Pu activity concentration and partitioning coefficients (LogKd) were strongly and positively correlated with nitrogen contents in both particulate and colloidal fractions. Results from solid state <sup>13</sup>C NMR suggest carboxylate functionalities contribute to the particulate-immobilization and colloidal-remobilization of Pu during HA37 groundwater resuspension. Carboxyl- and nitrogen-containing organic moieties in the bulk NOM pool served as the predominant Pu carrier, which is relevant to potential Pu mobility in natural soils during surface runoff events.

## Poster #165

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

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The Rocky Mountains of North America are experiencing a prolonged period of ecological stress resulting from coupled human and natural disturbances including logging, wildfire mitigation and incidence, climate change, and large scale insect infestation. The latter have decimated tree populations across millions of acres of forest in the region with repercussions for biogeochemical processes that can influence water resources, ecosystem function, and human well-being. The current exploratory project focuses on the decay of needle litter as a function of beetle impacted vs. unimpacted spruce (*Picea pungens*) in complement to lodgepole pine given their relevance to this form of large-scale disruption in the region. Needles were harvested from geographically similar sites and then deployed within the East River watershed at different elevations in fall 2016 to understand the effect of temperature, moisture, accelerated snowmelt and differing needle chemistry on decay processes and carbon and nitrogen export into the atmosphere (i.e. CO<sub>2</sub> and N<sub>2</sub>O) and hydrosphere (i.e. nitrate, ammonia, DOC). In isolating the needles from the hydrodynamic and biogeochemical variables of the tree system, our goal is to better understand the relative biogeochemical contributions of needle decay versus rhizospheric processes in distressed ecosystems. Ultimately this necessitates contrasting these processes with those under trees, where we propose to investigate plots of spruce trees in a nearby watershed that contains both beetle-killed and non-impacted spruce. In addition to enabling an understanding of these intertwined processes on biogeochemical cycling, this will enable us to query how localized treescale hydrologic and biogeochemical responses scale to watershed processes and the potential compensatory effects of healthy surrounding trees. Collectively, our research has implications for forest recovery and nitrogen export in this nitrogen-limited montane ecosystem and could aid in the prediction of and preparation for biogeochemical shifts that could impact water quality or greenhouse gas release.

**Poster #194**

**From Atomic Scale to Macroscopic Modeling: A Multi-Scale Framework for Mercury Biogeochemistry**

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Predicting the environmental fate and transport of mercury (Hg) in terrestrial surface and subsurface systems requires a thorough and accurate description of its speciation. Continuum-scale geochemical modeling typically employs experimentally determined thermodynamic binding constants (e.g., “log  $K$ ”) to model the transport and transformations of metals in the environment. However, the application of this method to Hg biogeochemistry is often limited due to the lack of reliable thermodynamic data. For example, the experimentally measured log  $K$  values for Hg complexation with highly variable natural organic matter (NOM) span a considerable range of >35 log units. Furthermore, even within a single well-defined system, such as Hg(Cys)<sub>2</sub>, literature values vary by >20 log units. To this end, we have generated an aqueous speciation database for Hg complexes by combining high-quality experimental data adherent to IUPAC standards with theoretical data calculated with density functional theory (DFT). Currently, the database includes over 500 experimental records for 152 inorganic and organic compounds, and continues to expand. We extend our previous work in applying DFT to predict the thermodynamic constants of Hg complexes uncertain or otherwise not available in the literature and integrate the results of 86 reactions calculated using 12 different DFT methods into the database. Further refinement of this database will provide a data resource for predicting speciation of Hg and other molecular species as well, and will therefore enable the application of the continuum-scale modeling to study Hg biogeochemistry. Future studies will focus on calibrating and improving the accuracy of the current DFT prediction model, and on linking the atomistic models to the macroscopic continuum-scale modeling framework to predict the transport and transformation of Hg in the environment.

## Poster #166

### PAF: A Cloud Based Framework for Site Monitoring

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Water resource management, agriculture and contaminated site remediation all require a timely understanding of subsurface processes to support operational efforts. This understanding requires the autonomous application of multi scale, multi domain models which are parameterized by heterogeneous multi scale data (geophysical, geochemical, hydrological and remote sensing) and the distillation of data and model outcomes into actionable information.

Under DOE SBIR award DE-SC0009732 Subsurface Insights in collaboration with LBNL scientists has developed the modular cloud based software framework PAF (Predictive Assimilation Framework) for providing this actionable information. PAF was designed from the ground up to provide a vertically integrated platform for all tasks ranging from heterogeneous data ingestion, qa/qc, data processing, parameter estimation, modeling, result sharing and information generation.

To achieve this PAF extensively leverages open source codes and capabilities for data ingestion, processing and modeling, including Landlab and PFLOTRAN (modeling), E4D (electrical geophysical data processing), ODM2 (Data storage), R (statistics), QGIS (data visualization and processing) and TikiWiki (knowledgebase).

Data is stored in a variety of ways including standard relational database (Mysql/PostGIS) and NoSQL solutions such as HDF5 data for storage of model results and Distributed Temperature Data. PAF uses configurable python workflows for back end tasks (such as data ingestion/harvesting and processing) which allows for rapid extension of capabilities as well as the use of the built in capabilities provided by Python for data processing and image manipulation. Within PAF, data and capabilities are exposed through APIs (either native to the open source component or developed in house) allowing for easy integration between components. PAF uses Zend Framework 2, a PHP 7 web application framework in the backend. Users interact with PAF through standard browsers and IOS and Android Apps. PAF is being developed and validated with data from different sites including the LBNL East River site. Specifically, we are currently extending PAF to include coupled surface/subsurface processes occurring between the bedrock and the soil/atmosphere interface. PAF: a cloud based framework for site monitoring



**Poster #167**

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

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This project is just beginning in 2017. We intend to combine multi-scale interdisciplinary strategies for improving the state of knowledge regarding the influence of deep-circulating groundwater on stream flows and stream-water chemistry in mountain watersheds. 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 an abundance of metal sulfide minerals in the aquifers, and can contribute substantially to stream chemical loads. We will compare how the fluxes of metals and other solutes to the surface varies between mineralized and unmineralized areas within the upper East River watershed and adjacent areas near Crested Butte, Colorado. This work will complement the ongoing ecohydrologic Science Focus Area (SFA) project led by the Lawrence Berkeley National Laboratory (LBNL) that includes extensive sampling and analysis of near-surface materials and surface waters by: (1) collecting new data in mineralized areas to contrast with the unmineralized East River study area, and (2) focusing on the contribution of deep-circulating groundwater and its geochemical composition to the shallow flow system. The 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 hydrogeologic system and help forecast the effects of perturbations such as climate change. We will combine new borehole installations with geologic, geophysical, geochemical, and hydrologic characterization of the deeper subsurface that extends 10s to 100s of meters below ground to better understand and quantify fluxes of water, metals, and other solutes from deeper to shallower environments.

## Poster #168

### **Hyporheic Mixing as a Strong Controller of Riverbed Biogeochemistry in Low-Order River Networks**

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Hyporheic mixing between river water and groundwater is hypothesized to exert a strong influence on riverbed biogeochemistry in low-order streams and rivers. Indeed, mixing zones near the sediment-water interface are thought to be hotspots of biogeochemical activity. In the semi-arid western US where river discharge is dominated by snow-melt, the seasonal expansion and contraction of the hyporheic zone likely exposes the riverbed to alternating oxic and anoxic conditions, with implications for reactions affecting metal mobilization and carbon processing. A greater understanding of these interdependent processes is critical for predicting the export of nutrients from upland watersheds, tracking metal mobilization in contaminated regions, and modeling the future behavior of river biogeochemistry in a changing climate.

Working around a representative meander feature of the East River (Crested Butte, CO), we used a series of vertically resolved temperature and redox probes to track the extent of hyporheic mixing, and the impact of mixing on riverbed biogeochemical processes. Pore water temperature data collected between August, 2016 and February, 2017 revealed a greater river water influence in the point bar location and a greater groundwater influence at the meander apex and cut bank locations. Groundwater upwelling increased at the cut bank location throughout the summer and fall. In winter, the onset of riverbed freezing occurred later at the groundwater-influenced locations, thus sustaining conditions necessary for microbial activity throughout more of the year. Further evidence for strong groundwater influence in shallow regions of the riverbed was obtained through depth-resolved pore water sampling at discrete time points. Characteristic of anaerobic microbial metabolism, aqueous metal (iron, manganese) concentrations increased with depth, while sulfate decreased over the same vertical profile. Furthermore, evidence of aerobic respiration (through oxygen consumption measurements) was mostly confined to the upper 20-cm of sediments. Ongoing 16S rRNA gene and metagenomic analyses will provide greater insight into the distribution of microbial metabolisms through the sampled zones.

In late-Spring 2017, complementary pore water samples will be collected during high river discharge to measure the effects of strong river water down-welling on riverbed biogeochemistry. Combined biogeochemical datasets will be used to develop coupled reactive transport and microbial population models in the riverbed. These models will be used to quantify reactive solute exchange across the riverbed and microbial population dynamics under various seasonal signals. In particular, we will explore potential impacts of future changes in precipitation, snowmelt, and river discharge on hyporheic mixing and associated biogeochemical processes.

## Poster #195

### Biogeochemical Release and Reactions of Iron-Bound Organic Carbon During the Redox Processes

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Iron (Fe)-bound organic carbon (OC) contributes an important component in the global cycles of OC. In this project, we have systematically studied the biogeochemical reactions of Fe-bound OC during the redox processes.

We have investigated the release and transformation of synthesized Fe-OC complexes during the abiotic and biotic reduction. During the abiotic reduction, hematite-bound OC was released more rapidly compared to the reduction of Fe, and aliphatic OC was more resistant to the reductive release than other components of OC. In the microbial reduction, reduction of ferrihydrite (Fh) and reductive release of Fh-bound OC were governed by the C/Fe ratio, with higher C/Fe ratio enhancing the Fe reduction and release of Fe-bound OC. In addition, we synthesized Fh coprecipitated with model OC, including glucose (GL), glucosamine (GN), tyrosine (TN), benzoquinone (BQ), amylose (AM), and alginate (AL). During the 25-d reduction by *Shewanella putrefaciens* CN32, the reductive release of OC followed the order Fh-BQ > Fh-GN > Fh-TN > Fh-GL > Fh-AL ≈ Fh-AM. OC regulated the reduction of Fh through acting as an electron shuttle and affecting the bacterial activity. Our results showed that the Fe reduction and release of Fe-bound OC were governed by the mineral phase of Fe oxide, C/Fe ratio, and chemical composition of OC.

For natural forest soils, Fe-bound OC contributed about 38% of total OC in forest soils. The anaerobic release of OC was closely related to the microbial reduction of Fe. When soils were transferred to aerobic conditions, the mineralization of OC was substantially inhibited compared to soils without pre-reduction. The OC was sequestered potentially through the co-precipitation with Fh formed during the oxidation of Fe(II). Oxidation of Fe(II) by O<sub>2</sub> led to the generation of OH radicals, which dominated the abiotic oxidation of OC. These findings provide a novel insight into the role of redox reactions in the biogeochemical cycles of OC. We also have monitored the seasonal dynamics of CO<sub>2</sub> and CH<sub>4</sub> for tundra soils at Toolik site, and analyzed the microbial community in these soils through 16S rRNA analysis.

Through experimental studies on the synthesized complexes and natural soils, our results uncover the coupled dynamics of Fe reduction and OC transformation, i.e. the release of OC during anaerobic reduction and inhibited mineralization under aerobic conditions. For the next step, we plan to study the long-term respiration of Fe-bound OC under different temperatures and transformation of different functional groups during the redox processes.

## Poster #196

### Investigating Greenhouse Gas Fluxes in Tundra Soils *in situ* in the Field and Under Controlled Laboratory Conditions

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Arctic tundra soils contain significant amounts of organic carbon that can potentially release greenhouse gases such as methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>), particularly during freeze-thaw cycles. As the atmospheric lifetime and radiative forcing of each of these species differs, it is important to understand the mechanisms by which carbon release may preferentially be in favour of one species over the other.

We present 2 years of *in situ* observations of CH<sub>4</sub> and CO<sub>2</sub> soil concentrations in the Arctic tundra at Toolik Field Station in northern Alaska by diffusive gas wells. Field observations show a consistent production of CO<sub>2</sub> in all six gas wells, including throughout the arctic winter at soil temperatures below -15°C. Field observations showed both net oxidation of CH<sub>4</sub> and production of CO<sub>2</sub> in tundra soils within close proximity. A critical observation was that the production of CH<sub>4</sub> continued throughout the arctic winter, but oxidation of CH<sub>4</sub> ceased during the coldest period, suggesting different temperature sensitivities of the two processes leading to changes in net ecosystem CH<sub>4</sub> production.

To further investigate temperature sensitivities for tundra CO<sub>2</sub> and CH<sub>4</sub> dynamics, we conducted controlled laboratory incubations studies using flux chambers whereby temperatures were shifted incrementally between -10 °C and 5 °C. Initial results show cessation all oxidation and production of greenhouse gases (GHG) below -1 °C, in contrast to field measurements that showed activity to continue under much colder temperatures. Net CH<sub>4</sub> fluxes altered with soil type and temperature, whereby O and A horizon soils showed net oxidation above 2 °C when thawing, yet the net oxidation flux continued below 1 °C during freezing. B horizon soil showed net CH<sub>4</sub> production above -1 °C when thawing, yet this flux stopped at 1 °C when freezing. These results show different temperature sensitivity of GHG production and oxidation in different soil horizons as well as differences between thawing and freezing processes.

## Poster #169

### Understanding Hydrobiogeochemical Drivers of Metal Export from Coal Creek, Colorado

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This project aims to develop predictive understanding of *key drivers of metal export at the watershed scale*. Metals association with dissolved organic carbon (DOC) is well documented at the laboratory scale. Preliminary data for Coal Creek, Colorado, have 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 (4.5% of the time), contributing disproportionately high fractions of 37% and 49% to the total annual water and DOC export, respectively. In this project we will 1) develop an integrated hydrobiogeochemical model at the watershed scale to systematically explore the connections among hydrological processes, soil carbon decomposition into DOC, and metal export; 2) apply the model to understand key drivers of metal export from Coal Creek.

In particular, we are developing a bioreactive module bio-RT to simulate processes including soil carbon stabilization, soil carbon decomposition into DOC, as well as complexation between DOC and metals. The module will be written in general framework and not for a particular watershed. All specifics of particular biogeochemical systems and watersheds will be communicated through input and output files. We will ultimately integrate bioRT into the IDEAS codes. 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.