2020
ENVIRONMENTAL SYSTEM SCIENCE (ESS)
VIRTUAL PRINCIPAL INVESTIGATORS MEETING

ABSTRACT BOOK

May 19-20, 2020

University-Led Research Abstracts
Extracted from Original Publication
2020 Environmental System Science (ES) Virtual Principal Investigators
Meeting

May 19-20, 2020

Organized by the U.S. Department of Energy, Office of Science, Office of
Biological and Environmental Research

Terrestrial Ecosystem Science (TES) Program
Program Manager:  Dr. Daniel Stover (daniel.stover@science.doe.gov)

Program Website:  tes.science.energy.gov/

Subsurface Biogeochemical Research (SBR) Program
Program Managers:  Mr. Paul Bayer (paul.bayer@science.doe.gov)
Dr. Jennifer Arrigo (Jennifer.arrigo@science.doe.gov)
Dr. Amy Swain (amy.swain@science.doe.gov)

Program Website:  www.doesbr.org/
Subsurface Biogeochemical Research

University Awards
Title: Seasonal origins of tree water-use along a hillslope in the East River Watershed

Max Berkelhammer1*, Gerald Page2, Christopher Still2, Lauren Hildebrand1, James Byron1, Kelsey Foss1.

1University of Illinois at Chicago, Chicago, IL;
2 Oregon State University, Corvallis, OR;

Contact: berkelha@uic.edu

Project Lead Principal Investigator (PI): Max Berkelhammer

BER Program: SBR

Project: University Project: Space and time dynamics of transpiration in the East River watershed: biotic and abiotic controls (DE-SC0019210)

Project Abstract:

Transpiration is a key component of the hydrological budget of the East River Watershed (ERW). Unlike evaporation, which can be estimated with some confidence using energetic constraints, transpiration is more complicated to model due to complex dynamics associated with root distributions and the stomatal response to atmospheric forcing. To provide constraints for future modeling, we developed continuous transpiration fluxes for three key species in the ERW (Picea engelmannii, Abies lasiocarpa and Populus tremuloides) along a ~500 m hillslope transect during 2019-2020. The observations show that the conifers have the highest levels of transpiration in late May and early June followed by a long-term decline through the end of the growing season. This progressive decline is interrupted by a modest increase in early August associated with a series of summer rain events. The seasonal trend largely mirrors surface soil moisture. On the other hand, the aspens show two transpiration peaks of similar magnitude in early July and early August. The largest transpiration fluxes appear to be around 3200 m, which marks an intermediate elevation between water-limitation at lower elevations and temperature-limitation at upper elevations. While the temporal dynamics seem to largely be explainable by seasonal trends in soil moisture, a lag emerges in July between the time of day when transpiration reaches its peak and the period of highest atmospheric evaporative demand, which shows how the stomatal response to atmospheric conditions further modulate transpiration. In addition to the transpiration measurements, we also measured the water isotopic ratio of the xylem water to understand the water sources the trees relied on. As expected, the trees almost exclusively utilized snow melt early in the growing season. As the season progressed, some trees transitioned into use of precipitation while others continued to use snowmelt through the entire growing season. Interestingly, snowmelt reemerged as the predominant water source across the hillslope at the end of the season reflecting either use of deeper waters or that older waters had migrated into the root zone as evaporative demand increased. Ongoing work includes tree-level modeling of transpiration using the Soil-Plant-Atmosphere (SPA) model, continuing the sap flux and isotopic measurements through the 2020 growing season, adding canopy-scale thermal imaging of the canopy to better understand leaf level processes and making measurements of the metal content in the xylem water to separate the current season’s snow melt from groundwater.
Title: The Hydro-bio-geochemistry of the Columbia River - Tributary Confluences

Thomas Bianchi,1* David Butman,2 Nicholas Ward,2-3 Michael Shields,4 Evan Arntzen,5 James Stegen,5 Julia Indivero,3 Yulia Farris,5 Albert Rivas-Ubach,6 Nikola Tolic,6 and Rosalie Chu6

1University of Florida, Gainesville, FL
2University of Washington, Seattle, WA
3Pacific Northwest National Laboratory, Sequim, WA
4Texas A&M University, College Station, TX
5Pacific Northwest National Laboratory, Richland, WA
6Environmental Molecular Sciences Laboratory, Richland, WA

Contact: (tbianchi@ufl.edu)

BER Program: SBR

Project: University Award: The Influence of Microbial Priming Effects on the Hydro-bio-geochemistry in the Columbia River and its Tributary Confluences

Project Website: Not applicable

Project Abstract:

River-tributary confluences, where diverse organic matter (OM) sources mix, are considered aquatic critical zones of biogeochemical cycling. The sources of OM to the Columbia River watershed are diverse, including dry land used for agricultural activity upstream from the McNary Dam and the Gifford Pinchot National Forest along the western reaches of the Cascades. Here we evaluate dissolved OM (DOM) composition and bioavailability in the mainstem of the Columbia River and four of its tributaries (Snake, Yakima, Walla Walla, and Wind rivers) in August 2018 and April 2019, respectively. We quantified concentrations of total dissolved organic carbon (DOC), total dissolved nitrogen (TDN), chromophoric dissolved organic matter (CDOM), dissolved lignin, dissolved hydrolysable amino acids, and examined the overall DOM molecular composition via Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS). DOC, TDN, and dissolved lignin concentrations were higher at most sampling locations in April when discharge was greater. Spatial and temporal variability in DOM composition was evident when examining the high-resolution mass spectrometry data along with the biomarker data via principal component analysis (PCA). For example, the Walla Walla River was relatively enriched in protein-like DOM in August but was enriched in dissolved lignin and phytochemical/oxyaromatic compounds in April. To assess bioavailability, field replicates and mixtures representing river-tributary confluences were incubated in the dark for 15 days. Total DOC significantly decreased only in a mixture representing the confluence of the Columbia and Walla Walla rivers sampled in August 2018. This was accompanied by a general decrease in dissolved lignin, but the decrease was not statistically significant. As mentioned above, the Walla Walla tributary was relatively enriched in protein-like DOM in August 2018. Therefore, it is possible this labile material primed the more stable Columbia River DOM. However, based on the insignificant decrease in dissolved lignin coupled with no significant changes in the compound class distribution measured via FT-ICR MS, the microbial community in the Walla Walla-Columbia mixture appeared to be indiscriminate of the molecular structure of the DOM.
Geophysical characterization of iron oxide precipitation in anoxic groundwater discharge zones

Chen Wang1*, Martin A. Briggs2, Frederick D. Day-Lewis2 and Lee D. Slater1
1Rutgers University, Newark, NJ;
2U.S. Geological Survey, Earth System Processes Division, Hydrogeophysics Branch, Storrs, CT;

Contact: (cw701@newark.rutgers.edu)

Project Lead Principle Investigator (PI): Martin A Briggs

BER Program: SBR

Project: University project

Project Website: (data releases)

http://doi.org/10.5066/P9Q1Z1TK; http://doi.org/10.5066/P9YWSJ2J; http://doi.org/10.5066/P931G95D

Project Abstract:

The precipitation of iron(III) oxides and/or hydroxides (Fe oxides) often occurs in streams and wetlands when low oxygen groundwater containing Fe(II) ions discharges into shallow oxygenated sediments and surface water. Efficient characterization of Fe oxide spatial distributions would permit identification of low oxygen groundwater discharge zones associated with contamination and enhanced biogeochemical reactions. Additionally, it would generate a better understanding of contaminant transport through river corridors as high surface area Fe oxides function as a sorption sink for dissolved contaminants (e.g., As, U). We aim to assess the spectral induced polarization (SIP) electrical geophysical technique for in situ and efficient characterization of Fe oxide precipitation in streambed sediments. We used laboratory experiments to show that the imaginary conductivity has a strong linear relationship ($R^2=0.87$) with sediment specific surface area, which in this case, is controlled by the concentration of fine-grained Fe oxides (up to 24.1 mg g$^{-1}$). We developed a specialized field measurement probe applied underwater to sense in situ the shallow streambed at up to 10 cm depth. We used a 1D analytical model to demonstrate the low sensitivity of the imaginary conductivity measurement to the electrically conductive stream water layer, a factor often complicating more typical electrical resistivity and electromagnetic measurements. We applied streambed SIP measurements along a coastal stream (Mashpee River, MA) and an alluvial river (East River, CO), where Fe oxide precipitates are formed by anoxic groundwater discharges resulting from a prior landfill leachate and beaver activities, respectively. We observed distinctly higher imaginary conductivity responses in the Fe oxide precipitation zones (up to 3 $\mu$S cm$^{-1}$) than the controlling background areas (generally less than 0.1 $\mu$S cm$^{-1}$). This study provides a new methodology for geolocating anoxic groundwater discharge zones and mapping spatial variations of sediment physicochemical properties.
The Effects of Stream Organic Matter on Respiration in Hyporheic Zones: Combined Insights from Flume and Computational Experiments

Anna Turetcaia\textsuperscript{1}, Bing Li\textsuperscript{2}, Xiaofeng Liu\textsuperscript{2}, Xingyuan Chen\textsuperscript{3}, Robert Danczak\textsuperscript{3}, Matthew Kaufman\textsuperscript{3}, Vanessa Garayburu-Caruso\textsuperscript{3}, Emily Graham\textsuperscript{3}, James Stegen\textsuperscript{3}, and M. Bayani Cardenas\textsuperscript{1,*}

\textsuperscript{1}The University of Texas at Austin, Austin, TX
\textsuperscript{2}Pennsylvania State University, State College, PA
\textsuperscript{3}Pacific Northwest National Laboratory, Richland, WA

(cardenas@jsg.utexas.edu)

**BER Program:** SBR  
**Project:** University award

Hyporheic zones (HZs) are a critical part of river corridors because of high rates of biogeochemical reactions which take place in them. The most important of these reactions is aerobic respiration because it is thermodynamically favored and it helps set up the redox ladder. This project’s goal is to improve the understanding of respiration in HZs. We ultimately seek predictive capabilities for the collection of HZ processes in system-scale models. The project is broadly divided into the intertwined tasks of advancing mechanistic models and the mapping and monitoring of reactions and the microbial communities responsible for these in real-scale laboratory flume experiments. Our most recent experiments are focused on determining how HZ respiration responds to perturbations in stream organic matter. In the flume, direct measurements of CO\textsubscript{2} production and O\textsubscript{2} consumption in both the overlying stream water and throughout the HZ sediment revealed that there is substantial respiration and that the rates vary with HZ depth. The experiments showed that the CO\textsubscript{2} in the stream, some of which is evaded to the atmosphere, is largely produced in the sediment and delivered to the channel by hyporheic exchange return flow. Computational flow and transport simulations, using the model we developed called hyporheicFoam which is based on the open-source model OpenFOAM, help explain the observed O\textsubscript{2} and CO\textsubscript{2} patterns. The simulations showed drastic gradients in the age of water flowing through the HZ. Most of the respiration happens in the shallowest HZ portion where the residence time is shortest and overlaps most with the respiration timescale and wherefrom the produced CO\textsubscript{2} is also easily expelled back to the stream. What therefore happened when stream organic matter increased was the respiration in the shallow HZ increased concurrently and linearly. As a consequence of the HZ-stream linkage, so too did the stream CO\textsubscript{2} concentration increase. Our study has shown that due to the strong coupling between the stream and the HZ, perturbations in stream dissolved organic matter are immediately felt within the HZ, which then quickly feedbacks to the stream. This new insight further highlights the importance of viewing the HZ and stream as a continuum, and that any predictive models will need to simultaneously and holistically consider these parts of the river corridor.
Trace Metal Dynamics and Limitations on Biogeochemical Cycling in Wetland Soils and Hyporheic Zones

Jeffrey G. Catalano¹*, Daniel E. Giammar¹, Jinshu Yan¹, Neha Sharma¹, Elaine D. Flynn¹, Grace E. Schwartz², Scott C. Brooks², Pamela B. Weisenhorn³, Kenneth M. Kemner³, Edward J. O’Loughlin³, Daniel I. Kaplan⁴

¹Washington University, Saint Louis, MO
²Oak Ridge National Laboratory, Oak Ridge, TN
³Argonne National Laboratory, Argonne, IL
⁴Savannah River National Laboratory, Aiken, SC

Contact: catalano@wustl.edu

Project Lead Principle Investigator (PI): Jeffrey G. Catalano

BER Program: SBR

Project: University Award

Project Abstract:

Biogeochemical cycling in subsurface aquatic systems is driven by anaerobic microbial processes. Many of the organisms involved mediate these processes using metalloenzymes that require trace metals as key reactive centers. Pure culture studies reveal that low availability of trace metals may inhibit methanogenesis, mercury methylation, and reduction of N₂O to N₂ during denitrification. However, whether such limitations occur in natural subsurface aquatic systems is currently unclear. If present, such limitations are likely controlled by trace metal speciation as this directly impacts bioavailability. This project seeks to establish mechanistic links between trace metal availability and biogeochemical carbon, nitrogen, and mercury transformations in subsurface systems. Integrated field and laboratory studies of trace metal availability and biogeochemical processes are underway at riparian wetlands in the Tims Branch watershed at the Savannah River Site and marsh wetlands at Argonne National Laboratory, both in collaboration with the Argonne Wetland Hydrobiogeochemistry SFA, as well as the streambed of East Fork Poplar Creek (EFPC) at Oak Ridge National Laboratory in collaboration with the ORNL Mercury SFA. Solid-phase trace metal (Co, Ni, Cu, Zn) concentrations in the soils and sediments at these sites are one-half to one-tenth of crustal averages. The overlying surface waters have dissolved trace metal concentrations roughly an order of magnitude below optimal levels for microbial processes. These observations suggest that our field sites will display metal-limited biogeochemistry. Despite the distinct physical settings under investigation, the speciation of trace metals in the wetland soils and stream sediments varied little, suggesting broadly universal controls on metal availability in subsurface aquatic systems. While the wetland soils and stream sediments displayed similar trace metal uptake behavior, added metals surprisingly formed different species at each site. Cobalt addition to stream sediments did not produce a clear impact on mercury methylation, but further studies are needed to examine longer incubation times. Ongoing incubations of wetland soils and stream sediments are investigating whether the addition of nickel and copper stimulate methanogenesis and N₂O reduction, respectively.
Title: Subalpine forest regeneration decreases DOM exports, but increases DOM reactivity to headwater streams

Tim Fegel¹*, Claudia Boot², Tim Covino², Kelly Elder¹, Ed Hall², Banning Starr¹, James Stegen³, Charles Rhoades¹
¹U.S. Forest Service, Rocky Mountain Research Station, Fort Collins, CO
²Colorado State University, Fort Collins, CO
³Pacific Northwest National Laboratory, Richland, WA

*Corresponding Author Contact Information:
U.S. Forest Service, Rocky Mountain Research Station 240 W. Prospect, Fort Collins, CO, 80526
Tel: 970-498-1017 email: timothy.fegel@usda.gov

Project Lead Principal Investigator (PI): Tim Covino

BER Program: SBR

Project: University project, Quantifying hydro-biogeochemical controls on watershed dissolved organic matter flux and processing

Project Abstract: The headwater forest ecosystems of the western U.S. generate a large portion of the dissolved organic matter (DOM) transported across North America. Land cover type, specifically tree species composition and structure in these headwater forests affect the quantity and characteristics of DOM transferred from terrestrial to aquatic ecosystems. Disturbance and management reset headwater forest species composition, with lasting effects on watershed carbon cycling. We investigated the role of forest land cover change between old growth and regenerating second-growth subalpine forest hillslopes in regulating the character and reactivity of DOM. Inputs of DOM derived from litter leachates and exports of DOM from lateral subsurface flow at the base of trenched hillslopes were evaluated during a three-year period (2016-2018) at the Fraser Experimental Forest in northcentral Colorado, USA. Differences in land cover type between old-growth and regenerating forest correlated with changes in DOM composition and reactivity. Subsurface flow draining the old-growth forest was higher in dissolved organic carbon (DOC) and total dissolved nitrogen (TDN). DOM composition from the old-growth forest had higher C:N ratio and was molecularly more complex and more aromatic than DOM from regenerating forest. DOM derived from the second-growth forest was more consistent with signatures of microbial processing. DOM from the second growth forest also had significantly higher biological oxygen demand (BOD) compared to the old-growth forest. Our findings demonstrate that changes in forest species composition and associated litter alter the composition and reactivity of DOM from litter and exports to adjacent aquatic ecosystems. Mixtures of old-growth and second-growth forests are common across headwater landscapes, and this study elucidates how these forest types drive a coupling between the composition and reactivity of DOM transferred from terrestrial to aquatic ecosystems.
Title: Simulating Snow Patterns and Evolution in the East River SFA with a Distributed Snow Dynamics Model

Jeffrey S. Deems,¹,² Mark Raleigh,¹ Gabriela Collao-Barrios,¹

¹ CIRES National Snow and Ice Data Center, University of Colorado, Boulder, CO;
² CIRES NOAA Western Water Assessment, University of Colorado, Boulder, CO;

Contact: (deems@nsidc.org)

Project Lead Principle Investigator (PI): Jeffrey S. Deems

BER Program: SBR

Project: University project

Project Abstract:

Spatial and temporal patterns of snow accumulation and melt exert a dominant control on hydrologic and biogeochemical flows in temperate mountain catchments. Mountain snowpack states, fluxes, and properties exhibit extreme and scale-dependent variability, complicating efficient sampling and modeling. Capabilities for evaluating the impacts of system perturbations (e.g. climate shifts, radiative forcing by impurities, forest cover change) on system water availability and nutrient cycling are contingent on robust observations and simulations of seasonal snow dynamics at appropriate scales of action.

To explore snow accumulation and melt process dynamics over the meter to watershed scales, we have implemented a physically-based snow cover evolution model (SnowModel; Liston et al., 2006) at multiple grid resolutions, using different combinations of accumulation process sub-models. We first tested the model in Senator Beck Basin, a well-instrumented study site in southwest Colorado. Model parameterizations for that site were then transferred to the East River SFA where instrumentation is less-reliable.

The simulations over a recent set of years spanning high and low peak accumulation values, were forced with high-resolution mesoscale model (WRF) and data assimilation model (HRRR) output, and are compared with ground measurements as well as snow depth and snow water equivalent (SWE) maps from Airborne Snow Observatory flights. These results help characterize the snow hydrologic system in the East River, and set the stage for future snow data assimilation work and for integration with simulations of connected systems within the SFA.

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

Jason Demers1*, Joel Blum1, Scott Brooks2, Elizabeth Crowther1 1University of Michigan, Ann Arbor, MI 2Oak Ridge National Laboratory, Oak Ridge, TN  
(jdemers@umich.edu)

Project Lead Principal Investigator (PI): Jason D. Demers BER Program: SBR
Project: University-Led Research Project Website: n/a

Historical and ongoing releases of mercury (Hg) have resulted in a legacy of Hg contamination in streambed sediment, streambanks, 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, streambanks, 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 suggest that additional dissolved Hg from the hyporheic pore water or groundwater discharge may variably contribute as much as a third of downstream dissolved Hg loads during baseflow conditions. Thus, the over-arching goal 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, drive observations of watershed-scale Hg fluxes, and result in bioaccumulation of methylmercury (MeHg).

To achieve this goal, we are combining a multi-seasonal field study with mechanistic laboratory experiments. First, we are coupling the Hg isotopic composition of dissolved Hg in stream water and in critical subsurface ecosystem compartments (i.e., hyporheic zone, riparian floodplains, and groundwater) with hydrologic fluxes in four reaches of EFPC to establish an isotope mass balance that assesses the relative importance of dissolved Hg contributed to the stream across these critical interfaces. Second, we are utilizing sequential extraction methods to characterize the isotopic composition of legacy Hg potentially re-mobilized from streambed sediment. This will provide insight into the sources and mechanisms that replenish the supply of dissolved Hg within critical subsurface zones. Third, we are assessing the isotopic composition of MeHg in biota of EFPC, as a step toward identifying the source(s) of bioaccumulative MeHg in the EFPC ecosystem.

Here, we present: (1) Hg concentration and isotopic composition of surface water, hyporheic pore water, and riparian groundwater; (2) isotopic mass balance assessments regarding legacy inputs of dissolved Hg to stream water of EFPC; and (3) Hg isotopic composition of sequentially extracted Hg from streambed sediment. We provide an overarching synthesis that shows: (i) recalcitrant fractions of legacy Hg in sediment is likely contributed to dissolved pore water and stream water; (ii) soluble sediment Hg fractions are likely derived from periphyton; and (iii) recalcitrant Hg released from legacy sediment may be incorporated into more soluble periphyton materials downstream along the flow path.
A Radioisotope-Enabled Reactive Transport Model for Deep Vadose Zone Carbon

Jennifer L. Druhan1*, Alison Tune,2 Jia Wang1, Corey R. Lawrence3, Jiamin Wan4, Daniella Rempe2

1Department of Geology, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA;
2Jackson School of Geosciences, University of Texas at Austin, Austin, Texas, 78705, USA;
3U.S. Geological Survey, Denver, Colorado 80225, USA;
4Lawrence Berkeley National Laboratory, Berkeley, California, 94720, USA

Contact: jdruhan@illinois.edu

Project Lead Principal Investigator (PI): Jennifer L. Druhan

BER Program: SBR

Project: University project

Project Abstract: In upland forested hillslopes such as the East River watershed, roots extend well beneath the classically defined soil layer into partially weathered, unsaturated rock to access both water and nutrients. Yet current carbon cycle models rarely extend below shallow soils, and the contribution of this deeper subsurface nutrient cycling to carbon stocks and fluxes is virtually unknown. In the Eel River watershed of Northern California, a team of SFA collaborators have successfully installed a novel Vadose zone Monitoring System (VMS) consisting of a pair of sub-horizontal bore holes instrumented with flexible plastic sleeves which allow sampling of fluids draining through the partially saturated shale weathering profile, as well as gas sampling ports, moisture and temperature sensors. Using this unique instrumentation, a DOE-SBR exploratory project (PI Druhan, DE-SC0019198) is now constraining carbon stocks and fluxes as an analog to the hillslopes of the East River, which is similarly underlain by a shale lithology and hosts mature forest ecosystems. These data provide new evidence that approximately 30% of net CO2 flux from the terrestrial environment to the atmosphere is sourced many meters below the soil layer (see A. Tune student poster for further details). Critically, the exploratory DOE-SBR grant has now shown that this CO2, though produced many meters below the soil, is radiocarbon modern. Thus, in total, this work indicates that modern carbon is being delivered rapidly to the deep subsurface, likely as a result of deep rooting zones, and this previously undocumented carbon cycle is a substantial component of the CO2 generated in the terrestrial environment. To extend these results, we have constructed a radioisotope-enabled version of the CrunchTope software which is now benchmarked as part of the exploratory proposal awarded to Dr. Druhan (Druhan et al., 2020). The new model is capable of simultaneous and explicit simulation of the three isotopes of carbon including both stable isotope fractionation and radioactive decay. Through this advanced modeling capability, the rates of carbon oxidation, contribution to weathering and thus the development of soils and sustainability of forest ecosystems will be embedded within an adaptive and predictive model framework.

Title: Deciphering controls on metal migration within floodplains: The critical role of redox environments on metal-organic complexes

Christian Dewey,1* Rene Boiteau,2 Marco Keiluweit,3 Scott Fendorf4

1Stanford University, Stanford, CA; 2Oregon State University, Corvalis, OR; 3University of Massachusetts; Amherst, MA

Contact: Fendorf@stanford.edu

Project Lead Principal Investigator (PI): Scott Fendorf BER Program: SBR

Project: University Project

Project Abstract: Dissolved organic matter (DOM) has a major but poorly understood control over the mobility of metals in surface and subsurface systems. Variations in the chemical composition of DOM across watersheds, owing to divergent organic matter transformation pathways, have potentially important influences on metal mobility. An outcome that has largely remained unexplored, but which may have critical impacts on dissolved metal concentrations and associated migration, is variation in the functional composition of DOM.

The overarching goal of our project is to determine the effect of redox conditions resulting from differing hydrologic environments on formation and transport of soluble metal-organic complexes. To meet our research goal, we developed a method to separate and quantify organic-metal complexes in natural DOM. We evaluated the role of column chemistry and solvent composition on elution and recovery of complexes of metals ranging in binding preferences (Al, Fe, Co, Ni, Cu, Zn, Cd, Pb) with (i) Suwannee River NOM and (ii) Suwannee River Fulvic Acid. Further, we examined variations in organic ligand binding of Cd from the DOE-sponsored East River Watershed using LC-ICPMS. Floodplain sediment pore-water samples were collected from oxic and anoxic environments and reacted with Cd. We observed significant differences in the composition of Cd binding ligands. In the oxic samples, three distinct Cd peaks are observed at early retention times, indicating different polar species. In the anoxic sample, the polar species are far less abundant and nonpolar ligands are observed. These results lead us to posit that redox environment, controlled by hydrologic state, is a major control over the composition of organic ligands across different regions of the watershed, and is consistent with the recent findings on the broader composition of organic matter across redox zones.

Our work is advancing a process-based understanding of metal fate and transport within watersheds, focusing principally on the dynamic hydrologic states of floodplains, leveraging the Columbia River, East River and Savannah River watersheds as experimental testbeds. Ultimately, our work is helping to advance the SBR programs goal of developing a robust predictive understanding of how hydrologic changes in watersheds affect water quality and inorganic element/contaminant loading.
Title: Metagenomic Insights into Key Nitrogen-Cycling Microbial Taxa within the Terrestrial Subsurface at Riverton, WY

Christopher A. Francis¹*, Linta Reji¹, Emily L. Cardarelli¹, Bradley B. Tolar, John R. Bargar², and Nicholas Bouskill³

¹ Department of Earth System Science, Stanford University, Stanford, CA
² SLAC National Accelerator Laboratory, Menlo Park, CA
³ Lawrence Berkeley National Laboratory, Berkeley, CA

Contact: caf@stanford.edu

Project Lead Principal Investigator (PI): Christopher Francis

BER Program: SBR

Project: University project DE-SC0019119

Project Abstract: Naturally-reduced zones (NRZs), formed within contaminated DOE legacy site floodplains in the upper Colorado River Basin, contain large inventories of nitrogen (N) and uranium (U). Microbial N-cycling processes, like nitrification and denitrification, have the capability to “unlock” the biogeochemical nutrient supply stored within NRZs, drive carbon cycling, and liberate U to the aquifers. However, despite their biogeochemical importance, remarkably little is known regarding N-cycling microbial communities within terrestrial subsurface sediments, let alone NRZs. To address this knowledge gap, we have performed detailed metagenomic analysis of microbial communities within sediment samples collected from the Riverton, WY subsurface. In particular, we have employed cutting-edge ‘binning’ approaches to generate metagenome-assembled genomes (MAGs) from 12 subsurface depths within a ~2.4 m sediment depth profile. This resulted in the generation of 100s of draft- to high-quality MAGs, many of which correspond to N-cycling taxa. Since our recent work highlighted the importance of ammonia-oxidizing archaea (AOA) in the Riverton subsurface (based on N-cycling functional genes and 16S rRNA amplicon sequencing), a major goal of this project was to definitively link key AOA functional genes (e.g., amoA, nirK, etc.) to their corresponding 16S rRNA sequences through the analysis of thaumarchaeal MAGs. Our binning efforts resulted in over 20 distinct thaumarchaeal MAGs spanning 11 different depths. Phylogenetic analysis of these genomes, based on ribosomal proteins and multiple functional genes, revealed truly remarkable AOA diversity. Interestingly, comparison of these MAGs to reference genome sequences revealed that, while some genomes were most closely related to known terrestrial AOA (e.g., Nitrososphaera, Nitrosocosmicus), others either represent completely novel lineages or are most closely to AOA from aquatic and even marine environments. We also observed islands of AOA gene clusters unique to Riverton MAGs. Interestingly, pangenome analysis revealed a clear distinction between AOA genomes derived from ‘above’ versus ‘below’ the water table, highlighting the underappreciated importance of hydrology in controlling AOA distribution and diversity in this environment. Finally, several nitrite-oxidizing bacterial genomes (e.g., Nitrospirota) were also obtained (containing nxr genes), which likely oxidize the nitrite produced by AOA to nitrate in these sediments. Overall, this project is yielding unprecedented genomic and ecophysiological insights into the microbial communities responsible for N-cycling, and especially nitrification, in a terrestrial subsurface environment that is directly influenced by hydrological fluctuations.
Physical, Biological and Resource Supply as Key Factors Driving Nutrient Uptake Along a Fluvial Network

Jancoba Dorley1*, Ricardo González-Pinzón1, Dave Van Horn2

1Department of Civil, Construction and Environmental Engineering, University of New Mexico, Albuquerque, New Mexico
2Department of Biology, University of New Mexico, Albuquerque, New Mexico

Contact: (gonzaric@unm.edu)

Project Lead Principal Investigator (PI): Ricardo González-Pinzón

BER Program: SBR

Project: University Project

Project Abstract: Nutrient impairment has led to damages to US surface and groundwater systems in excess of 100 billion dollars per year. Therefore, there is a strong need to develop methods to predict the transport, uptake, and export of nutrients along fluvial networks. We present results that are based on a data-driven mechanistic understanding of three factors that largely control nutrient uptake and export: 1) interactions between transport-related processes (mass transfer to metabolically active zones), 2) resource supply dynamics (nutrient concentration, Stoichiometric constraints, etc.), and 3) biological controls (microbial community structure and function). Our results were generated from column experiments conducted along the Jemez River-Rio Grande continuum which spans four orders of magnitude in mean annual discharge, more than 2000 m in altitude, and more than 500 km of stream longitude. Two resource supply injections were performed on each of the columns, i.e., a nitrate only addition, followed by a stoichiometrically ‘balanced’ 106Carbon:16Nitrogen:1Phosphorus addition. We quantified NO3-N uptake kinetics while constraining three variables: stream order, sediment type and type of injection(N vs stoichiometrically ‘balanced’ C:N:P) throughout the river continuum. We observed increases in NO3-N uptake velocity for the Stoichiometrically ‘balanced’ injection relative to concentrations during the Nitrate only injection, except for the 1stand one of the 7thOrder sites (downstream of a Wastewater Treatment Plant). Higher NO3-N uptake velocities were also observed in the Native sediment compared to the sterile sediments. We also observed that limitation and co-limitation in biological NO3-N across the two-injection experiments varied with stream order. Lastly, the Michaelis-Menten asymptotic decay pattern was observed for NO3-N uptake kinetics. While our results shows that stoichiometric imbalances limits nutrient uptake in lotic systems, ongoing work with our partners at the Pacific Northwest National Laboratory (PNNL) is seeking to identify how the type of microbial communities sampled from each of the columns control the observed uptake results.
Resolving Aquifer Controls on Larger River-Groundwater Exchanges of Mass and Energy

Michael Gooseff1*, Xingyuan Chen2, Martin Briggs3, Neil Terry3, Evan Arntzen2

1University of Colorado, Boulder, CO; 2Pacific Northwest National Laboratory, Richland, WA; 3Hydrogeophysics Branch, US Geological Survey, Storrs, CT;

Contact: michael.gooseff@colorado.edu

Project Lead Principle Investigator (PI): Gooseff
BER Program: SBR
Project: University Project

Streams and rivers exchange water with surrounding aquifers preferentially through permeable geologic units. These exchanges of water between the surface and subsurface are important vectors of energy, biota, and solutes. They support fisheries and the removal of some pollutants from rivers. When submerged they are invisible to the naked eye, and to date, we have a poor understanding of the geologic controls on these exchanges in large river settings, hampering the development of predictive models. The overarching goal of this research project is to determine whether the dominant controls on groundwater inflows to rivers lie at the bed of the river or underneath the riverbed. Riverbeds are rarely smooth, regardless of their make-up (fine sediment versus gravel). Bedforms are generated in patterns that reflect the energy of the moving water in the channel. Across these bedforms, moving river water experiences shear stress, which can “pump” water into and out of the riverbed. Beyond the riverbed and its shorelines, the geologic setting of a river strongly dictates the river form (sinuosity and slope for example), as well as the potential patterns of water movement between the surface and subsurface. Current work along the Columbia River corridor being completed by scientists at the Pacific Northwest National Laboratory includes modeling convective exchange of river water through the bed and banks, broader groundwater flow modeling, and the collection of shallow geophysics data to characterize the distribution of near-surface geologic deposits that might influence river-groundwater exchange. In this research, we seek to identify groundwater inflows to the Columbia River using established and emerging field techniques adopted for large channels, and determine whether they are associated with the geologic structure around the river or the convective exchange along the riverbed. We will collect deep geophysical data using a FloaTEM system, which is a new cutting-edge tool for towed investigations.

This research will significantly complement the PNNL Scientific Focus Area research project on river corridors. Our findings will help put into context the processes occurring immediately adjacent to river channels, and help discriminate between proximal and distal controls. Our findings will also be useful for informing and calibrating reactive transport models being developed by other science groups working along the Hanford Reach of the Columbia River. The findings will also advance our fundamental understanding of the connections of landscapes to large river systems, which has potentially significant implications for water and fisheries management practices.
Methylation Potential of Mercury for Different Groups of the Methylating Microbial Community

Heileen Hsu-Kim¹, Natalia Neal-Walthall¹, Austin Wadle¹, Caitlin M. Gionfriddo², Dwayne Elias², Cynthia C. Gilmour³
¹ Duke University, Department of Civil & Environmental Engineering, Durham, NC
² Oak Ridge National Laboratory, Oak Ridge, TN
³ Smithsonian Environmental Research Center, Edgewater, MD

Contact: (hsukim@duke.edu)

Project Lead Principal Investigator (PI): Heileen Hsu-Kim

BER Program: SBR

Project: University project

Project Website: N/A

Project Abstract:
Methylmercury (MeHg) is a highly bioaccumulative form of mercury (Hg), and the mitigation of risk at contaminated sites requires tools to quantitatively predict MeHg production. This study examined the factors influencing microbial methylation of mercury (Hg) in freshwater wetland ecosystems with the goal of developing geochemical and biomolecular markers for net MeHg production potential. We are testing the hypothesis that mercury methylation potential in sediments can be predicted through a combination of diffusive gradient in thin-film (DGT) passive samplers (for bioavailable Hg flux) with genomic analysis of Hg-methylating microbial communities. We constructed three simulated freshwater wetlands in an outdoor field research station at Duke University. Each mesocosm comprised a 3.7×1.2×0.8 m³ (length×width×height) slant-bottom box, filled with soil and water to create a gradient of water saturation conditions and was populated with freshwater macrophytes, mosquitofish, and associated macrofauna. After establishment of the simulated wetlands, each mesocosm box was amended with four different geochemically relevant and isotopically labelled inorganic Hg species to represent a gradient of different Hg methylation potentials across the four isotopes. Over several months, after the initial spike of mercury forms in the wetland mesocosms, we monitored each isotopically labelled Hg endmember for: (1) Accumulation into water, sediment and biological components in the mesocosm; (2) Conversion to MeHg in water and sediments; and (3) Accumulation of total Hg and MeHg on DGTs deployed for one week periods in the mesocosms. The results showed that most of the added Hg from each isotope accumulated in the top few centimeters of surface sediment in the first month after dosing. Greater conversion to MeHg was generally observed for the isotopes originating from dissolved forms ($^{202}$Hg$^{2+}$, $^{201}$Hg-humic acid complex) than for isotopes originating from particulate forms (nanoparticulate $^{200}$HgS and $^{199}$Hg adsorbed to FeS). Also, the uptake of inorganic Hg in DGTs were generally consistent with trends for methylated Hg, indicating that DGT passive samplers might be useful as an empirical tool to evaluate Hg bioavailability for methylating organisms. Ongoing work will attempt to establish changes in the sediment microbial community during the 12-month period after Hg dosing, and compare to the observed changes in the extent of Hg methylation during this time frame.
Title: Root Influences on Mobilization and Export of Mineral-bound Soil Organic Matter

Marco Keiluweit1*, Zoe G. Cardon2, Malak Tfaily3, Hui Li1, Mariela Garcia-Arredondo1, Rosalie Chu4, Rene Boiteau5, Yilin Fang6, Steve Yabusaki6

1University of Massachusetts, Amherst, MA 2Marine Biology Laboratory, Woods Hole, MA 3University of Arizona, Tucson, AZ 4Environmental Molecular Science Laboratory, Richland, WA 5Oregon State University, Corvallis, OR 6Pacific Northwest National Laboratory, Richland, WA

Contact: (keiluweit@umass.edu)

Project Lead Principal Investigator (PI): Marco Keiluweit

BER Program: SBR

Project: University project (exploratory)

Project Website: NA

Project Abstract: Biogeochemical cycles within mountainous watersheds are key regulators of ecosystem carbon storage and downstream nutrient loadings, and they have shown to be particularly vulnerable to climate change impacts. Increasing temperature and persistent droughts have already dramatically changed vegetation cover across the mountainous western US, with unknown consequences for carbon and nutrient cycles in soils belowground. What remains elusive is to what extent associated changes in root-soil interactions may mobilize the vast pool of organic matter (OM) that has been stabilized by associations with minerals for centuries or millennia. Although plant root-driven OM mobilization from minerals may be a central control on carbon loss and nutrient export, such mechanisms are currently missing from conceptual and numerical models. The overall objective of this project is to identify the biogeochemical mechanisms by which roots destabilize mineral-OM associations and the cumulative impact on carbon and nutrient fate. To accomplish this goal, we integrated model system and greenhouse experiments with a scalable modeling approach. We conducted model system experiments to assess the vulnerability mineral-associated organic matter (MAOM) to exudate-mediated mechanisms. Our results show that common root exudates effectively destabilize MAOM not only through direct, ligand-driven mobilization mechanisms, but also indirect, microbially-mediated mechanisms relying on secondary metabolites and enzymes. We further found that OM bound to poorly crystalline Fe and Al (hydr)oxides is more vulnerable to exudate-induced destabilization than OM bound to more crystalline phases, particularly in response to direct, ligand-promoted mechanisms. These findings demonstrate that the stability of MAOM is not just a function of their inherent properties, but also will depend in large parts on the ability of plant roots and microbes to produce exudates capable of triggering suitable mobilization mechanisms. We further employed a well-controlled rhizobox approach, combined with advanced microsensor and mass spectrometry techniques, to resolve spatiotemporal variations in the composition and availability of exudates along single growing roots of grasses. We show that the composition of functionally relevant exudate compounds varies at extremely short time scale, seemingly shifting from ligands such as aromatic acids around root tips to less reactive metabolites such as amino acids around mature root segments. These results suggest a prevalence of direct MAOM mobilization mechanisms around the root tip, while indirect MAOM mobilization strategies may dominate around more mature root segments. Finally, employing parallel microsensor measurements of moisture, redox, oxygen, and pH dynamics in the rhizosphere, we parameterized a rhizosphere (hydro)biogeochemistry reactive transport model. The resulting model was used to assess how transient changes in (hydro)biogeochemical properties of the rhizosphere affect that stability of MAOM. Simulations suggest that diel pulses in root exudation are strong enough to significantly destabilize MAOM. We will further
highlight ongoing field-based experiments aiming to quantify the impact of MAOM mobilization across the subalpine East River watershed. In sum, results from our integrated experiment-modeling project highlights the strong control plant roots exert on the stability of MAOM and, thus, on the potential for carbon and nutrient export from watersheds.
Title: Watershed scale seismic imaging and porosity estimation with the seismic land streamer in the Upper East River, Colorado

James St. Clair¹, Lee M. Liberty¹

¹Boise State University, Boise, ID

Contact: (lliberty@boisestate.edu)

Project Lead Principal Investigator (PI): Lee Liberty

BER Program: SBR

Project: Boise State award DE-SC0019224

Project Abstract:

The East River Watershed Science Focus Area is a DOE funded experimental watershed dedicated towards developing a predictive understanding of hydrologic and biogeochemical processes within mountain watersheds. Bedrock in the watershed is composed of Mancos Shale and younger crystalline intrusions. Hillslopes are mantled with weathered bedrock, moraines, landslides and colluvium. During October of 2018 we conducted a watershed scale seismic survey of the drainage. The dataset includes ~12 km of data collected along roads with a 72-channel, 1.25m spaced streamer and ~3km of planted geophone data. P-wave (Vp) and shear wave (Vs) results reveal a sharp transition between regolith/sediment deposits and bedrock throughout the watershed. This sharp velocity contrast produces a high amplitude secondary arrival, which travels at the expected bedrock Vs. We interpret this arrival as a vertically polarized shear wave and use it to constrain bedrock Vs. Mancos Shale Vp anisotropy is measurable in some parts of the watershed and notably absent in the vicinity of crystalline intrusions. This suggests contact metamorphism influences bedrock hydrology. Hertz-Mindlin derived porosity estimates measurements show relatively high porosities within alluvial and colluvial (up to 0.5) deposits compared to bedrock (less than 0.05), in agreement with borehole observations. Localized, low Vp anomalies in the bedrock correlate with regional fracture sets visible in Lidar data, however their limited vertical extent suggests that permeability along these fractures decreases rapidly with depth. We also observe bedrock Vp trends that correlate strongly with local shale dip, bedrock Vp is slowest where the Mancos Shale dips into hillslopes and fastest where the shale dip is parallel to the hillslope. These results suggest shale structure strongly influences bedrock hydrology.
Distinct Source Water Chemistry Shapes Contrasting Concentration-Discharge Patterns

Wei Zhi¹, Li Li², Wenming Dong³, Wendy Brown⁴, Jason Kaye⁴, Carl Steefel³, Kenneth H. Williams³,⁴

¹Department of Energy and Mineral Engineering, The Pennsylvania State University, University Park, PA
²Department of Civil and Environmental Engineering, The Pennsylvania State University, University Park, PA
³Earth and Environmental Sciences Area, Lawrence Berkeley National Laboratory, Berkeley, CA
⁴The Rocky Mountain Biological Laboratory, Crested Butte, CO
⁵Department of Ecosystem Science and Management, The Pennsylvania State University, University Park, PA

Project Lead Principal Investigator (PI): Li Li, SBR University project DE-SC0016221, collaboration with the Watershed Function Science Focus Area at Lawrence Berkeley National Laboratory funded by the DOE SBR under the contract DE-AC02-05CH11231

Project Website: Li Reactive Water Group

Contact: (lili@engr.psu.edu)

Abstract Understanding concentration-discharge (C-Q) relationships are essential for predicting chemical weathering and biogeochemical cycling under changing climate and anthropogenic conditions. Contrasting C-Q relationships have been observed widely, yet a mechanistic framework that can interpret diverse patterns remains elusive. This work hypothesizes that seemingly disparate C-Q patterns are driven by switching dominance of endmember source waters and their chemical contrasts arising from subsurface biogeochemical heterogeneity. We use data from Coal Creek, a high-elevation mountainous catchment in Colorado, and a recently developed watershed reactive transport model (BioRT-Flux-P1HM). Sensitivity analysis and Monte-Carlo simulations (500 cases) show that reaction kinetics and thermodynamics and distribution of source materials across depths govern the chemistry gradients of shallow soil water and deeper groundwater entering the stream. The alternating dominance of organic-poor yet geo-solute-rich groundwater under dry conditions and organic-rich yet geo-solute-poor soil water during spring melt leads to the flushing pattern of dissolved organic carbon and the dilution pattern of geogenic solutes (e.g., Na, Ca, and Mg). In addition, the extent of concentration contrasts regulates the power law slopes (b) of C-Q patterns via a general equation \( b = \frac{\delta b}{C_{ratio}} + b_{min} \). At low ratios of soil water versus groundwater concentrations \( (C_{ratio} = C_{sw} / C_{gw} < 0.6) \), dilution occurs; at high ratios \( (C_{ratio} > 1.8) \), flushing arises; chemostasis occurs in between. This equation quantitatively interprets b values of 11 solutes (dissolved organic carbon, dissolved P, NO3, K, Si, Ca, Mg, Na, Al, Mn, and Fe) from three catchments (Coal Creek, Shale Hills, and Plynnlimon) of differing climate, geologic, and land cover conditions. This indicates potentially broad regulation of subsurface biogeochemical heterogeneity in determining C-Q patterns and wide applications of this equation in quantifying b values, which can have broad implications for predicting chemical weathering and biogeochemical transformation at the watershed scale.

Reference:
Development of a molecularly informed biogeochemical framework for reactive transport modeling of subsurface carbon inventories, transformations and fluxes

Kate Maher1*, Matthew J. Winnick1,2, Dana K. Chadwick1, Hsiao-Tieh Hsu1, Yuchen Liu3, Jennifer L. Druhan3, Corey R. Lawrence4

1 Department of Earth System Science, Stanford University, Stanford, California 94305, USA
2 Department of Geosciences, University of Massachusetts Amherst, Amherst, MA 01003
3 Department of Geology, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA
4 U.S. Geological Survey, Denver, Colorado 80225, USA

Contact: kmaher@stanford.edu

Project Lead Principal Investigator (PI): Kate Maher

BER Program: SBR

Project: University Project

Project Abstract: Soils moderate the two largest fluxes in the carbon cycle: plant uptake of atmospheric CO2 through photosynthesis and the resulting heterotrophic and autotrophic respiration that returns CO2 to the atmosphere. Imbalances in these fluxes can thus substantially alter global carbon budgets and promote positive feedbacks in the climate system that are not well resolved in large scale climate models. The flux of carbon between the vegetation and the atmosphere is moderated by the soil organic carbon (SOC) reservoir, which is highly sensitive to shifts in (1) water availability and (2) vegetation dynamics. To address the potential for moisture-driven feedbacks, the overarching goal of our project is to develop new techniques to quantify soil organic carbon transformations that support development of new models of carbon (and nutrient) transfers to and from the soil reservoir.

To quantify the controls on depth-resolved net CO2 production rates and the spatial variability in SOC inventories and guide model development, we are using field measurements of soil respiration, soil pCO2 and SOC content in tandem with remote sensing data across the unique field laboratory of the East River, CO watershed, in collaboration with the Lawrence Berkeley Lab SFA. An inverse 1-D diffusion-reaction model constrained by soil pCO2 and surface efflux rates was developed to calculate net CO2 production rates ($R_{CO2}$) over time. Field measurements are accompanied by laboratory incubation experiments and a meta-analysis of literature studies to assess theoretical constructs needed to accurately capture the response of microbial respiration to variable soil moisture. In both field and laboratory studies, East River soil profiles demonstrate unique responses to precipitation events, and accurate prediction of the associated respiration of carbon requires a sophisticated modeling approach. To capture this behavior, we have built a ‘dormancy model’ which allows the native soil microbial population to respond transiently to the presence or absence of water. However, field measured $R_{CO2}$ show a dampened respiration response to moisture delivery when plants are senesced, suggesting that vegetation status is also important control on soil respiration. Collectively, our results suggest that plant phenology regulates the response of soil respiration rates to pulse wetting events. In particular, these results emphasize the importance of the timing of snowmelt and the summer monsoon relative to phenology on soil CO2 fluxes and their sensitivity to projected changes in climate.
Transport and Retention of Metal Reducing Motile Bacteria in Idealized Pore Geometries

Lazaro Perez¹, Rishi Parashar¹*, Nicole Sund¹, Andy Plymale², Timothy Scheibe²

¹Desert Research Institute, Reno, NV
²Pacific Northwest National Lab, Richland, WA

Contact: rishi@dri.edu

Project Lead Principal Investigator (PI): Rishi Parashar

BER Program: SBR

Project: University led EPSCoR Project

Project Abstract:

For several species of motile microorganisms, encompassing strictly anaerobic, facultatively anaerobic, and facultatively autotrophic bacteria, with capacities to reduce a range of metals and radionuclides, micromodel experiments were conducted in idealized pore networks under both flow and no-flow conditions. The micromodels were designed as chambers with small depth (10 µm and 20 µm) and properties of bacterial transport and retention (biofilm formation) were studied in the horizontal plane. The density of the bacterial solution was kept low to minimize the interaction between individual cells. Videos of bacterial motion were recorded at various magnifications and frequencies. Trajectories of individual cells ranging from several seconds to few minutes in duration were extracted in neutral conditions (in the absence of any chemical or redox gradient). Position of individual cells in the videos were found by filtering the difference in pixel intensity between the current video frame and the mean image over the duration of the video. Groups of pixels in the species size range were merged to estimate the location of the cell center. Locations of cell centers were connected to create motion paths, which were extracted by categorizing cells based on their previous speed. Cell trajectories that were collected from the videos were then analyzed to determine the suitability of Fickian and non-Fickian transport models as a function of timescale and pore structure. Growth of biofilm in the micromodel was studied which includes determination of biofilm morphology and its relation to pore structure, and its effect on fluid properties such as porosity, velocity, and development of preferential channeling. The micromodel experiments and related model to study motile microorganisms’ transport and retention is expected to provide pathway for development of methodologies to include upscaled bacterial motion properties in bioremediation implementations.
Influence of hyporheic exchange on coupled S-Fe-C biogeochemical cycling in riparian wetland sediments

Cara M. Santelli¹, Crystal Ng¹, Shreya Srivastava¹, Aubrey Dunshee¹, Daniel Kaplan³, Kenneth Kemner⁴, Maxim Boyanov⁵

¹University of Minnesota, Minneapolis, MN
²Northwestern University, Evanston, IL
³Savannah River National Laboratory, Aiken, SC
⁴Argonne National Laboratory, Argonne, IL
⁵Bulgarian Academy of Sciences, Sofia, Bulgaria

contact: santelli@umn.edu

Project Lead Principal Investigator (PI): Cara Santelli

BER Program: SBR

Project: University Award

Riparian wetland hyporheic zones, where oxic surface water and anoxic groundwater mix, exhibit spatiotemporally dynamic conditions that drive steep redox gradients and promote hotspots of diverse and fluctuating microbial activity. Growing evidence suggests that highly active “cryptic” sulfur redox processes drive the fate of iron and carbon in riparian wetlands including the production of reactive intermediate S species that promote further biotic and abiotic redox reactions such as those coupled with Fe reduction and methane oxidation, thus supporting higher rates of sulfur biogeochemical cycling than otherwise expected in these low sulfate environments. As “cryptic” sulfur redox processes are not well constrained in freshwater systems, much uncertainty remains as to how these processes affect the fate of Fe and CH₄ and respond to dynamic hyporheic fluxes in natural field settings. The overall goal of this research is to develop a mechanistic understanding of coupled biotic-abiotic Fe-S-C cycles in hydrologically dynamic wetland sediments. One of our specific objectives is to evaluate the microbial community structure and potential function driving these cycles. 16S rRNA and fungal internal transcribed spacer (ITS) sequencing was used to investigate the microbial communities inhabiting 6 different sites in an organic-rich riparian wetland at Tims Branch, part of the Argonne Wetland Hydrobiogeochemistry SFA. Preliminary results reveal a diverse microbial community dominated by phyla Proteobacteria, Acidobacteriota, Chloroflexi and Actinobacteriota. Fungal communities were dominated by Ascomycota, Mortierellomycota and Basidiomycota in these sediments. Seasonal variations in geochemical and hydrologic conditions and sediment depth affected the relative abundance of these phyla. For example in wetland sediments under gaining stream conditions, aqueous iron increased at depth, the relative abundance of Crenarchaeota decreased substantially at those depths in both January and August. In January, sulfate concentrations in the wetland sediments decreased at the top 0-5 cm interval and then increased at greater depths, which was reflected in a decrease in the relative abundance of sulfate-reducing Desulfobacterota from shallower to deeper depths. Despite an opposite trend in sulfate concentrations in the wetland sediments in August as a result of hyporheic fluxes, an opposite trend was not observed for the relative abundance of Desulfobacterota suggesting a potential role of abiotic Fe-S cycling processes. These results indicate that hyporheic fluxes and fast redox processes impact microbial distribution. Further work, with respect to this objective will focus on correlating hydrological and geochemical parameters with microbial community structure and function to acquire a deeper understanding of the role microbes play in Fe-S-C cycles in these wetlands.
Title: Constraining Physical Understanding of Aerosol Loading, Biogeochemistry, and Snowmelt Hydrology from Hillslope to Watershed Scale in the East River Scientific Focus Area

S. McKenzie Skiles*, 1 David Gochis, 2 Janice Brahney, 3

1 University of Utah, Salt Lake City, UT;
2 National Center for Atmospheric Research, Boulder, CO;
3 Utah State University, Logan, UT

Contact: m.skiles@geog.utah.edu

Project Lead Principal Investigator (PI): S. McKenzie Skiles

BER Program: SBR

Project: University Project

Project Abstract:

The mountain snowpack is a critical component of regional hydrology, ecology, biogeochemistry, and climate in the Western US. This project leverages the East River Scientific Focus Area (SFA), as an outdoor laboratory to address a significant gap in our understanding of the mountain snowpack; namely, how atmospheric constituent deposition on snowpack influences snow energy balance and nutrient/chemical cycling, and how snowmelt timing and intensity exerts controls on emergent biogeochemical and ecohydrologic behavior. This aligns with East River SFA goals to integrate landscape scale measurements and physical based modeling tools to improve understanding of controls on runoff production, ecohydrology, biogeochemical cycling, and land surface energy partitioning in high mountain watersheds. We will present current observation and results from the project, including observations of snowpack at multiple scales such as surface elevation and snow reflectance measurements from NASA-JPL’s Airborne Snow Observatory, high-resolution measurements of snow and deposited aerosols physical, chemical, and optical properties, and discuss future planned observations for tracking of deposited aerosols residence and reaction times in the watershed, and in situ time series of surface energy balance, water flux, and water chemistry. We will also highlight how we plan to fuse the remotely sensed and ground based measurements with an operational, physics-based hydrologic model, the WRF-Hydro/National Water Model system, to test and improve its capability to represent alpine snow dynamics, and related control on ecohydrologic and biogeochemical processes, from the hillslope to watershed scale.
Computational Models of Dissolved Organic Matter

Jeremy C. Smith,1,2* Deepa Devarajan,1,2 Scott C. Brooks,2 Scott L. Painter,2 Baohua Gu,2 Jerry M. Parks2, Liyuan Liang1,2

1 University of Tennessee Knoxville, TN 2 Oak Ridge National Laboratory, Oak Ridge, TN Contact: (smithjc@ornl.gov)

Project Lead Principle Investigator (PI): Jeremy C. Smith

BER Program: SBR Project: University project

Dissolved organic matter (DOM) plays a significant role in the biogeochemical processes of the aquatic and terrestrial environments including the global carbon cycle, microbial metabolism, transport of nutrients and contaminants. DOM is a complex heterogeneous mixture of several organic units. Molecular level interactions between those component molecules are responsible for active roles of DOM. Therefore, it is important to understand the behavior of DOM at the atomistic/molecular level. Here, molecular dynamics (MD) simulations were used to explore the interactions between the component molecules of DOM. Model lipid, peptide, carbohydrate, lignin, and low molecular weight organic compounds were simulated along with cations in water for 200ns. Various components of DOM aggregate to form dynamic supramolecules consisting of a hydrophobic core and an amphiphilic exterior. The molecular surface of DOM is composed of both hydrophobic and hydrophilic groups allowing DOM to bind with polar and non-polar molecules. DOM models for Leonardite humic acid and Suwanee River DOM were constructed and validated based on their elemental compositions and other available properties. The DOM models will be used to estimate the physiochemical properties for the biogeochemical reactions of DOM. Further refinement of the DOM models will involve increasing the variety of building block molecules.
Integration of Omics into a New Comprehensive Rate Law for Competitive Terminal Electron-Accepting Processes in Reactive Transport Models: Application to N, Fe, and S in Stream and Wetland Sediments

Martial Taillefert1,* (PI), Eryn Eitel1, Thomas DiChristina2 (co-PI), Hyun-Dong Shin2, Frank Stewart2 (co-PI), Anthony D. Bertagnolli2, Nastassia V. Patin2, Kenneth Kemner3 (Co-PI), Scott Brooks4 (Co-PI), Christa Pennacchio5, and Stephen J. Callister6

1School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332 2School of Biological Sciences, Georgia Institute of Technology, Atlanta, GA 30332 3Biosciences Division, Argonne National Laboratory, Argonne, IL 60439

4Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

5Joint Genome Institute, Walnut Creek, CA 94598

6Environmental Molecular Science Laboratory, Richland, WA 99354

Contact: (mtaillef@eas.gatech.edu)

Project Lead Principal Investigator (PI): Martial Taillefert

BER Program: SBR

Project: University Project

Project Abstract: The dynamic of biogeochemical processes regulating nutrient and contaminant release in stream and wetland sediments and their role in carbon transformation cannot be predicted accurately by current reactive transport models (RTMs). These models largely rely on detectable changes in geochemical conditions to activate metabolic processes, are unable to accurately account for competition between microbial processes, and poorly constrain the effect of hydrological perturbations on biogeochemical processes. The objectives of this project are to: (i) develop new rate laws for RTMs that rely on a combination of high throughput omics (meta-genomic, -transcriptomic, -proteomic, -bolomic) and geochemical signatures to identify the underlying anaerobic microbial processes in stream and wetland sediments; (ii) describe the competition between the dominant metabolic processes involved in contaminant (U and Hg) mobilization; and (iii) more accurately quantify carbon transformation processes. A combination of meta-omic and geochemical signatures were used to identify the main anaerobic microbial processes in a Savannah River Site wetland (SRS) and Oak Ridge East Fork Poplar Creek (EFPC) sediment. Geochemical depth profiles suggested that Fe(III) reduction dominates carbon remineralization processes in SRS wetland sediments, whereas a combination of NO3− and Fe(III) reduction dominates EFPC sediments. Sediment slurry incubations designed to investigate the competition between anaerobic terminal electron accepting processes demonstrated that NO3− reduction was the fastest respiratory process and that Fe(III) reduction apparently became dominant once NO3− was depleted. Incubations also revealed that SO42− reduction was inhibited by Fe(III) reduction and that this inhibition was enhanced by ferricydrate addition. In turn, metagenomic signals were enriched in gene variants indicating that bacteria coupling anaerobic ΣH2S oxidation to NO3− reduction were dominant in EFPC sediments but not in SRS wetland sediments. Metagenomic data thus indicate that a cryptic sulfur cycle may be more significant than apparent by geochemical signals. The metagenomic data is currently being confirmed via complementary meta-transcriptomic and -proteomic analyses. A gene-centric kinetic model was developed that includes a set of new...
rate laws to represent competition between microbial communities involved in carbon remineralization processes. The model calibrated with one set of incubations was able to reproduce all the incubation treatments, suggesting that it could be readily included in RTMs. Overall, this project demonstrates that: (i) a combination of high throughput omic and geochemical data is needed; and (ii) simple gene-centric models can be readily included in RTMs to accurately identify biogeochemical processes and the competition between microbial communities involved in contaminant transformation in sediments.
Decrease in Aqueous U(VI) Following an Influx of Oxidants into Organic-Rich Reduced Sediments

Karrie A. Weber¹², Jeffrey P. Westrop¹, Pooja Yadav¹, Vincent Noel³, Arjen Van Veelen³⁴, John R. Bargar³, Romy Chakraborty⁵

¹University of Nebraska-Lincoln, Lincoln NE
²Daugherty Water for Food Institute, Lincoln, NE
³SLAC National Accelerator Center, Menlo Park, CA
⁴Los Alamos National Laboratory, Los Alamos, NM
⁵Lawrence Berkley National Laboratory, Berkley CA

Contact: kweber@unl.edu

Project Lead Principal Investigator (PI): Karrie A. Weber

BER Program: SBR

Project: University Project

Project Abstract: An existing paradigm describes that the influx of oxidants such as dissolved oxygen (DO) or nitrate will stimulate the oxidation of reduced chemical species such as iron, Fe(II), and uranium, U(IV). The change in redox state thus alters metal/radionuclide behavior and contributes to the generation of soluble and mobile U(VI) species influencing contaminant mobility. Field research results challenged the existing paradigm whereby low concentrations of an oxidant (DO) were directly amended into an alluvial aquifer and stimulated reducing conditions as well as a decrease in aqueous uranium concentrations (Rifle, CO; (Pan et al., 2018)). A series of laboratory experiments was initiated in batch reactors containing reduced, organic-rich, uranium bearing alluvial sediments (collected from Riverton, WY; SLAC SFA) test the impact of the influx of low oxidant concentrations (nitrate and DO) on uranium mobility. These reduced sediments were amended with anoxic bicarbonate buffered medium (Ar:CO₂, 80:20; pH 6.7) with and without the addition of an oxidant (nitrate or DO). Aqueous U concentrations decreased (KPA and ICP-MS) following the addition of the oxidant, nitrate or DO. No significant decrease in aqueous U(VI) concentrations were observed in unamended controls. XANES analysis revealed an increase in solid-associated U(VI) in DO amended reactors. However, the inverse was true in nitrate amended reactors. XANES analysis of sediments collected from nitrate amended reactors revealed an increase in the amount of U(IV) relative to the unamended controls (85% U(IV) in treatment relative to 31% U(IV) in control). In addition to observing the reduction of uranium, a significantly higher concentration of aqueous Fe(II) was also observed in treatments relative to an unamended control indicating active Fe(III) reduction. Concurrent with an increase in aqueous Fe(II), a decrease in sulphide was observed. While this result could be indicative of oxidation, PHREEQC modelling of geochemical data supports the precipitation of Fe-sulphide as a potential mechanism for sulfide loss. All geochemical changes were observed concurrent with an increase in cell and virus abundance indicating cell growth and microbial activity. No significant changes were observed in controls. Together these results indicate that U retention under oxidizing conditions may not be solely limited to solid-phase sequestration of U(VI) but also an influx of an oxidant such as nitrate that can stimulate U(VI) reduction leading to sequestration as U(IV). This challenges our current understanding of U mobility in natural systems and indicates overlooked controls governing U redox cycling.

Using Global Sensitivity Analysis to Identify Controlling Processes of Complex Systems
Ming Ye,1,* (Presenting Author), Li Li,2 Xingyuan Chen,3

1Florida State University, Tallahassee, FL; 2Pennsylvania State University, State College, PA; 3Pacific Northwest National Laboratory, Richland, WA

Contact: Ming Ye(mye@fsu.edu)

BER Program: Subsurface Biogeochemical Research

Project: University-Led Research

Project Web: https://atmos.eoas.fsu.edu/~mye/DOE_ProcessIdentification.php

Project Abstract:
This project developed three new methods of global sensitivity analysis for identifying controlling processes of an environmental system that is always open and complex. For such a system, understanding all its processes and their interactions is difficult. On the other hand, since the system dynamics are determined mainly by controlling processes, efforts should be spent to better understand the controlling processes, and on the other hand, spending efforts on non-influential processes should be avoided. These are challenging because of uncertainty inherent in system processes. This project considers process model uncertainty (i.e., a process can be represented by more than one process model) and process parametric uncertainty (i.e., a process model parameter is not deterministically known but follows a distribution). The overarching scientific question to be answered in this project is as follows: If we are not certain about the choice of process models and model parameters, can we correctly identify the controlling processes of a complex system? We developed three methods of global sensitivity analysis to tackle this question from different angles (theoretical and computational).

The first approach was developed for process prioritization to identify the process(es) that should be better understood to achieve the greatest reduction in the uncertainty of the output of system modeling. We developed a process sensitivity index, which is conceptually similar to the first-order sensitivity index of the Sobol’ method. During this project, we developed a new computational method to substantially reduce the computational cost of calculating the process sensitivity index by reducing the computational cost from $N^2$ model runs to $2N$, where $N$ is on the order of hundreds to thousands.

The second approach was developed for process fixing to screen non-influential process(es) with small contribution to the uncertainty of the output of system modeling. We developed a total process sensitivity index, which is conceptually similar to the total-effect sensitivity index of the Sobol’ method. We evaluated this sensitivity index by using analytical functions and numerical groundwater models with three model uncertainty in the processes of land surface recharge, subsurface geology, and river boundary. This sensitivity index was also implemented using the computationally efficient method discussed above.

To further reduce the computational cost of process fixing, we developed the third approach that extends the design of Morris method for model parameters to model processes. Our methods reduces the number of model runs from thousands to tens, and the results are consistent with those of the total process sensitivity index discussed above,