

**2019 ENVIRONMENTAL SYSTEM
SCIENCE PRINCIPAL INVESTIGATORS
MEETING
ABSTRACT BOOK**

April 30 - May 1, 2019
Bolger Center, Potomac, MD

University-Led Research
Abstracts Extracted
from Original
Publication

2019 Environmental System Science Principal Investigators Meeting

April 30 – May 1, 2019

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. Amy Swain (amy.swain@science.doe.gov)

Program Website: www.doesbr.org/

AAAS Fellow: Dr. Jessica Moerman (Jessica.moerman@science.doe.gov)

Subsurface Biogeochemical Research

University Awards

Poster #21-18

Forest Stress in the Rocky Mountains During the Last Interglacial Warm Period

Max Berkelhammer^{1*}

¹ University of Illinois Chicago, Chicago, IL

Contact: berkelha@uic.edu

BER Program: SBR

Project: University Award

Growing season temperature is a key determinant of forest stress in the Western United States, which portends reductions in growth, including the possibility of regional forest die-off, as temperatures continue to rise. Here, we look at the ecohydrological effects of warming on Western US forests using interglacial-aged subfossil conifer wood samples from Colorado, USA. New downscaled climate model simulations for this period show canopy warming of ~2-4 degrees and an earlier retreat of snowpack, yet our analyses of the carbon isotopes and tree growth show little evidence of enhanced stress levels relative to today. Results from the oxygen isotope ratios in the sub-fossil cellulose show that an increased utilization of summer rain by the trees compensated for the detrimental forcing associated with higher temperatures. The study shows that changes in summer rain, which are notoriously difficult to model, can alter the trajectory of western US forests even in regions that fall outside of traditional monsoon regimes. A detailed analysis of root water uptake dynamics of conifers will be undertaken in the East River Watershed during the 2019 growing season using a new network of sap flow sensors and water isotope analysis.

Poster #21-56

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

Thomas Bianchi^{1*}, David Butman², Nicholas Ward²⁻³, Michael Shields¹, Evan Arntzen⁴, James Stegen⁴, Julia Indivero³, Yulia Farris⁴, Albert Rivas-Ubach⁵, Nikola Tolic⁵, and Rosalie Chu⁵

¹ University of Florida, Gainesville, FL

² University of Washington, Seattle, WA

³ Pacific Northwest National Laboratory, Sequim, WA

⁴ Pacific Northwest National Laboratory, Richland, WA

⁵ Environmental Molecular Sciences Laboratory, Richland, WA

Contact: tbianchi@ufl.edu

BER Program: SBR

Project: University Award

A positive priming effect occurs when the microbial oxidation of terrestrial dissolved organic matter (TDOM) is enhanced by the addition of algal dissolved organic matter (ADOM). However, the prevalence of priming within river-tributary confluences, with often contrasting OM sources and composition, remains unknown. Here, we measure total dissolved organic carbon, dissolved nitrogen, chromophoric dissolved organic matter, dissolved lignin phenols, dissolved hydrolysable amino acids, and the molecular composition of DOM via FT-ICR-MS in the mainstem of the Columbia River and three of its tributaries (Snake River, Yakuma River, and Walla Walla) along an extreme hydrologic east-west gradient in the Columbia River drainage basin. Field replicates and mixtures representing river-tributary confluences were incubated in the dark for 15 days to investigate the response of the microbial community to varying DOM quantity and composition. The Columbia, Snake River, and Yakuma Rivers did not differ in DOC, fDOM, and chlorophyll-a concentrations. However, Walla Walla tributary had significantly greater DOC, fDOM, and chlorophyll-a concentrations, indicative of greater contributions from ADOM than the Columbia River and these other tributaries. The FT-ICR-MS spectra for Walla Walla had significantly more peaks corresponding to amino sugars, carbohydrates and proteins while the Columbia River had more peaks for lignin, unsaturated hydrocarbons, and condensed aromatics. When incubated for 15 days in the dark, the DOC did not decrease for Walla Walla or any of the other river and tributary samples. The DOC did decrease, however, in a mix representing the confluence of the Columbia and Walla Walla rivers, suggesting the microbial consortia of the Columbia River were primed by the Walla Walla DOM. The DOM composition, measured by the number of peaks detected via FT-ICR-MS, were significantly different for several compound classes (lignin, protein, tannin, etc.) in the incubations of unmixed river and tributary samples. However, the primed microbial community in the Walla Walla-Columbia mixture appeared to be indiscriminate of the molecular structure of the DOM as the peak count for each compound class did not change significantly. This provides preliminary evidence that the enzymes exuded during aquatic priming can hydrolyze diverse OM structures. Overall, our results indicate the presence of microbial priming effects generated by confluences that mix contrasting OM quality.

Poster #21-61

Methane and Nitrous Oxide Pore-Water Concentration and Flux at the Hyporheic Zone of a Large River

Jorge A. Villa^{1*}, Garrett Smith¹, Lupita Renteria², James Stegen², Kelly Wrighton³, and Gil Bohrer¹

¹ Ohio State University, Columbus, OH

² Pacific Northwest National Laboratory, Richland, WA

³ Colorado State University, Fort Collins, CO

Contact: villa-betancur.1@osu.edu

BER Program: SBR

Project: University Award

Greenhouse gas (GHG) emissions from rivers are a critical missing component of current global GHG models. Their exclusion is mainly due to a lack of in-situ measurements and to a poor understanding of the spatiotemporal dynamics of GHG production and emissions which prevents optimal model parametrization. In this project, we are conducting data-driven field research on the hyporheic zone of a river shore section of the Columbia River. We aim to understand at an ecosite scale: (i) where and when are GHGs produced and if the production is impacted by river stage, (ii) what microbial processes control production and consumption of GHGs and, (iii) what is the effect of environmental conditions on GHG production at the Columbia River nearshore environment and what is the scale in which they operate and could be best modeled. We are using a multidisciplinary approach combining pore dialysis peepers to determine pore water concentration of GHGs, co-located GHG flux measurements with non-steady-state accumulation chambers, meta-omics of microbial communities in the sediment profile to identify microbial processes, and modeling to scale and interpret the observations. We have installed nine peepers in three transects covering shallow, intermediate and deep-water levels. Measurements of pore water concentration of methane (CH₄) and nitrous oxide (N₂O), and co-located flux measurements, were conducted during three different hydrological conditions (rising, falling and falling highly-regulated river stages). Overall, integrated CH₄ porewater concentrations along the sediment profile followed a pattern similar to that of CH₄ fluxes for the three water levels of the gradient during the hydrological conditions considered. However, hotspots in porewater concentrations occurred at different depths in the profile, indicating the influence of groundwater mixing in the patterns observed. In turn, N₂O porewater did not show discernible patterns for the hydrological conditions, and fluxes did not show statistical differences along the gradient of water levels. The next steps in our study are to link concentration and flux results with metagenomic and metatranscriptomic data to help explain the patterns observed (or lack thereof), and parametrize the biogeochemical model *ecosys* to represent individual microbial processes and evaluate their scaling across depths and spatially distinct sites. We expect that our findings help improve predictive understanding of how watersheds function as complex hydrobiogeochemical systems. We also envision that data and results generated in this project will benefit reactive transport models of microbial carbon cycling that can be integrated into the U.S. DOE ACME Land Model (ALM).

Respiration in Hyporheic Zones: Advancing the Understanding of Coupled Transport and Microbial Biogeochemistry and their Representation in Open-source Mechanistic Models

M. Bayani Cardenas^{1*}, Xiaofeng Liu², Xingyuan Chen³, Stephen Ferencz¹, Matthew Kaufman³, Bing Lu², Anna Turetaica¹, Joseph Brown³, Yilin Fang³, Emily Graham³, Maoyi Huang³, and James Stegen³

¹ The University of Texas at Austin, Austin, TX

² Pennsylvania State University, State College, PA

³ Pacific Northwest National Laboratory, Richland, WA

Contact: cardenas@jsg.utexas.edu

BER Program: SBR

Project: University Award

Hyporheic zones (HZs) are a key feature of river corridors because of substantial carbon and nutrients processing which happen in them. This processing is a cascade of microbially-mediated reactions. The most important of these reactions is respiration since it is thermodynamically favorable and the consumption of oxygen during respiration sets up a cascading redox ladder.

This project's goal is to improve the understanding of respiration in HZs. We seek predictive capabilities that can represent 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. The flume experiments use real river water and have been continuously running for months. Direct measurements of CO₂ production and O₂ consumption in both the overlying channel water and throughout the HZ sediment reveal that there is substantial respiration and that the rates vary with HZ depth. The distribution of respiration-sensitive reactive tracers independently support the occurrence of respiration. Microbial community characterization shows that the communities in the flume are similar to those in natural river settings. The communities occupying oxic and anoxic zones are distinct. The experiments show that the CO₂ in the channel, which presumably is evaded to the atmosphere, is largely produced in the sediment and delivered to the channel by hyporheic return flow. This finding emphasizes the importance of considering the HZ, the channel and the overlying atmosphere as one continuum with fully, two-way coupled components. Thus, we are also advancing the modeling of processes that transcend the sediment-water-air interfaces. The model we have developed is called *hyporheicFoam* which is based on the open-source model OpenFOAM. It solves the Reynolds Averaged Navier-Stokes and modified Richards equations for the turbulent open-channel flow and flow in the porous sediment respectively. It takes user-specified biogeochemical reaction networks. Just as we observed in the flume experiments, modeling with *hyporheicFoam* showed that CO₂ produced from respiration in the HZ is released to the channel and eventually to the atmosphere. Our observational and modeling study is the first to show these facets of HZ respiration. Future plans include experimental and modeling assessment of the many factors which control HZ respiration including different forms and sources of carbon and varying hydraulic conditions. The results of this sensitivity analysis will be synthesized into quantitative predictive models.

Poster #22-30

Trace Metal Dynamics and Limitations on Biogeochemical Cycling in Wetland Soils and Hyporheic Zones

Jeffrey G. Catalano^{1*}, Daniel E. Giammar^{1*}, Elaine D. Flynn¹, Jinshu Yan¹, Neha Sharma¹, Grace E. Schwartz², Scott C. Brooks², Pamela B. Weisenhorn³, and Kenneth M. Kemner³

¹ Washington University, Saint Louis, MO

² Oak Ridge National Laboratory, Oak Ridge, TN

³ Argonne National Laboratory, Argonne, IL

Contact: catalano@wustl.edu

BER Program: SBR

Project: University Award

Aquatic ecosystems display strong coupling between hydrologic conditions and the cycling of carbon, nitrogen, and other major elements as well as trace metal micronutrients and contaminants. In many such systems, sharp redox gradients can produce spatially-varying regions of biogeochemical activity. The biogeochemistry of subsurface zones of aquatic systems has been widely explored from the perspective of redox conditions, substrate availability, and thermodynamic controls on metabolic processes. However, an additional yet under-examined constraint is the availability of trace metal micronutrients. An array of metalloenzymes are essential to many biological pathways associated with microbial carbon and nitrogen cycling and mercury methylation. Laboratory studies using isolate microorganisms have demonstrated that low metal availability inhibits key biological pathways, but similar limitations in natural and human-impacted systems have not been widely investigated. The project thus seeks to establish whether aquatic systems display trace metal limitations on biogeochemical carbon, nitrogen, and mercury transformations. We hypothesize that solid-phase speciation is the primary control on metal availability and that biogeochemical processes utilizing a pathway containing a single, metal-bearing enzyme are most susceptible to metal limitations. This project integrates field and laboratory studies of trace metal availability and biogeochemical processes occurring in wetland soils and hyporheic zone sediments. Our primary field sites include a riparian wetland 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 hyporheic zone of East Fork Poplar Creek (EFPC) at Oak Ridge National Laboratory in collaboration with the ORNL Mercury SFA. These studies are supplemented by work in marsh wetlands at Marais Temps Clair Conservation Area near St. Louis, MO. In the first half- year of this project, our efforts have focused on key initial tasks. Preliminary measurements showed that the addition of nickel to incubations of marsh soil increased methane production by a factor of 10. We have pursued similar studies using stream sediments from EFPC to explore whether cobalt addition affects mercury methylation. No clear trend was observed, but future work will examine longer incubation times. Soil, sediment, and water sampling at both the EFPC and marsh wetlands at Argonne have investigated the controls on trace metal availability. Planned sampling at the Tims Branch riparian wetland along with incubation experiments using materials from all field sites will further assess the impact of trace metal availability on biogeochemical cycling.

Poster #21-17

Quantifying Subsurface Biogeochemical Variability in a High Altitude Watershed During Winter Isolation

Jessica Buser¹, Laura Lapham¹, Andrew Thurber¹, Kenneth Williams¹, and Frederick Colwell¹

¹ Oregon State University, Corvallis, OR

Contact: rcolwell@coas.oregonstate.edu

BER Program: SBR

Project: University Award

Subsurface ecosystems in high-altitude watersheds are influenced by hydrologic events that drive the availability of compounds for biotic and abiotic chemistry. Much of this biogeochemistry occurs in the dynamic hyporheic zone (the interface of the river sediment and groundwater) and in groundwater. Hyporheic systems are conspicuously responsive to hydrologic events, and therefore have the ability to alter surface ecosystem geochemistry. High-altitude systems experience isolation during the wintertime due to unsafe or inclement conditions that prevent access to the watershed for research, and consequently many of these systems are not sampled during the winter months. This isolation leads to a distinct gap in biogeochemical knowledge of these systems, which ultimately affects the accuracy and confidence in which these systems are computationally modeled. We deployed and subsequently retrieved OsmoSamplers from the East River (ER), CO watershed to study the aqueous and gaseous chemistry of the waters from the aquifer, river, and hyporheic zone during the winter. Our Shumway well sampler detected ca. 10x higher concentrations in Cl^- at the end of winter than during the rest of the year, adding to data previously collected only when the well could be accessed. The sampler also validated sustained low levels of SO_4^{2-} in groundwater through late fall and winter months showing an upward trend as summer started. Methane in the well was near saturating levels through the year. Our 10-month sampler installments in the ER surface water revealed up to 50 μM levels of methane in July through September, an increase compared to ca. 5 μM during most months. In contrast, samples from 20-cm deep in the hyporheic zone showed a spring-to-early summer peak in methane (< 65 μM) before declining. A second set of OsmoSamplers is being used to study the microbiome and metatranscriptome of the ER system. These measurements aim to accurately capture the biogeochemistry of the dynamic hyporheic ecosystem's response to hydrologic seasonality in high-altitude watersheds, strengthening our understanding of these systems during the winter months.

Poster #21-63

Persistent Effects of Forest Harvest on Dissolved Organic Matter Composition in Subsurface Hillslope Runoff

Tim Fegel¹, Banning Starr¹, Kelly Elder¹, Tim Covino^{1*}, Ed Hall¹, Claudia Boot¹, and Charles Rhoades¹

¹ Colorado State University, Fort Collins, CO

Contact: tim.covino@colostate.edu

BER Program: SBR

Project: University Award

Timber harvesting commonly alters soil nitrogen (N) and carbon (C) inventory and associated biogeochemical processes the initial years after treatment, yet changes in critical zone processes as forests recover from harvesting remain poorly understood. In high-elevation conifer forests of the Rocky Mountains, slow tree growth and short growing season prolong post-harvest ecosystem responses. Here we analyze hillslope-scale subsurface flow at the Fraser Experimental Forest to evaluate differences in nutrient export and dissolved organic matter (DOM) composition between old-growth and second-growth forest more than three decades after clear cut harvesting. Runoff passing through the upper 3 m of the soil profile was collected before, during, and after peak subsurface discharge during 2017 and 2018. In the second-growth stand, runoff nitrate concentrations were significantly higher and dissolved organic C concentrations were lower relative to the old-growth forest. Dissolved organic N was an order of magnitude higher than dissolved inorganic N concentrations in both forest conditions. Fluorescence spectroscopy of subsurface flow showed contrasting DOM composition from the old- and second-growth forests. The old-growth forest was composed of more complex, aromatic DOM and microbial-like DOM was more prevalent in the second-growth forest. Subsurface flow C:N ratios were twice as high in the old-growth forest and correlated with DOM characterization indices based on fluorescence spectroscopy. Further, biological oxygen demand assays showed that DOM exported from the second-growth forest was consumed 50% more rapidly than that from the old-growth forest. Old-growth and second-growth forests are common within managed landscapes and this hillslope scale comparison will advance understanding of long-term changes in critical zone processes that regulate watershed C and N export and downstream water quality.

Poster #21-15

Snow Accumulation and Melt Simulations in Dry Through Wet Years in the East River

Jeffrey S. Deems^{1*} and Mark S. Raleigh¹

¹ CIRES National Snow and Ice Data Center, University of Colorado

Contact: deems@nsidc.org

BER Program: SBR

Project: University Award

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 are implementing a physically-based snow cover evolution model (SnowModel; Liston et al., 2006) at multiple grid resolutions, using different combinations of accumulation process sub-models, over a recent set of years spanning high and low peak accumulation values. These simulations, forced with high-resolution mesoscale model (WRF) output, are compared with ground measurements as well as snow depth and snow water equivalent (SWE) maps from Airborne Snow Observatory flights. These initial 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.

Reference:

Liston, G.E., Elder, K., 2006. A Distributed Snow-Evolution Modeling System (SnowModel). *J. Hydrometeorol.* 7, 1259–1276.

Poster #22-36

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

Jason D. Demers^{1*}, Joel D. Blum¹, Scott C. Brooks², and Elizabeth R. Crowther¹

¹ University of Michigan, Ann Arbor, MI

² Oak Ridge National Laboratory, Oak Ridge, TN

Contact: jdemers@umich.edu

BER Program: SBR

Project: University Award

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 comparing hydrologic discharge and THg flux from Y12 and Lower EFPC 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 the bioaccumulation of methylmercury (MeHg).

To achieve this goal, we are combining an intensive 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 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.

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 all surface water, hyporheic pore water, and riparian groundwater samples analyzed to date; (2) isotopic mass balance assessments regarding legacy inputs of dissolved Hg to the stream water of EFPC; (3) sequential extraction results showing potential re-mobilization of recalcitrant legacy Hg from streambed sediment; and (4) measurements of the isotopic composition of MeHg accumulating in biota of EFPC.

Poster #21-16

A Radioisotope-Enabled Reactive Transport Model for Deep Vadose Zone Carbon

Jennifer L. Druhan^{1*}, Alison Tune², Jia Wang¹, Corey R. Lawrence³, Jiamin Wan⁴, and Daniella Rempe²

¹ University of Illinois at Urbana-Champaign, Urbana, IL

² University of Texas at Austin, Austin, TX

³ U.S. Geological Survey, Denver, CO

⁴ Lawrence Berkeley National Laboratory, Berkeley, CA

Contact: jdruhan@illinois.edu

BER Program: SBR

Project: University Award

In upland forested hillslopes, such as those observed across 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. We are now directly constraining this previously disguised component of the carbon cycle through a novel Vadose zone Monitoring System (VMS) installed at the Eel River watershed in Northern California, which is similarly underlain by a shale lithology and hosts a mature forest ecosystem. The VMS consists of a pair of sub-horizontal bore holes instrumented with flexible plastic sleeves which allow both passive and active suction cup sampling of fluids draining through the partially saturated shale weathering profile, as well as gas sampling ports, moisture and temperature sensors. Our exploratory efforts are now constraining carbon stocks and fluxes as an analog to the hillslopes of the East River, providing new evidence that approximately 30% of net CO₂ flux from the terrestrial environment to the atmosphere is sourced many meters below the soil layer. We have shown that this CO₂, though produced well below what would classically be defined as 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 the rooting depth of mature trees, and this previously undocumented carbon cycle is a substantial component of the CO₂ generated in the terrestrial environment. To extend these results, we are now working with the LBNL SFA team to generate comparable datasets of CO₂ and O₂ gradients, complementary fluid phase DIC and DOC, and radiocarbon to constrain the contribution of deeply rooted vegetation to this subsurface carbon cycle. Modeling will be supported by the radioisotope-enabled version of CrunchTope, capable of simultaneous and explicit simulation of the three isotopes of carbon including both stable isotope fractionation and radioactive decay. Model development has been completed and aspects have been benchmarked against several other multi-component software platforms. 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.

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

Christian Dewey^{1,2}, Carolyn Anderson³, Hannah Naughton¹, Rene Boiteau⁴, Peter Nico², Markus Kleber⁴, Scott Fendorf^{1*}, and Marco Keiluweit²

¹ Stanford University, Stanford, CA

² Lawrence Berkeley National Laboratory, Berkeley, CA

³ University of Massachusetts-Amherst, Amherst, MA

⁴ Oregon State University, Corvallis, OR

Contact: Fendorf@stanford.edu

BER Program: SBR

Project: University Award

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 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.

Using a combination of field-scale measurement with micro-scale laboratory experiments, we find that oxygen diffusion limitations lead to heterogeneous redox profiles, shifting microbial metabolism to less efficient anaerobic SOC oxidation pathways. During flooded periods, exhibiting strongly reducing conditions, DOC concentrations are elevated yet microbial C oxidation is limited by thermodynamic constraints on anaerobic respiration. Through laboratory incubations, we observed both kinetic and thermodynamic controls on carbon oxidation; anaerobic incubations were tested with nitrate and sulfate addition relative to an anoxic control and compared against aerobic conditions. Under anaerobic conditions, oxidation rates are consistent with thermodynamic succession in energy yields. Carbon oxidation rates are, however, highly sensitive to oxygenation, particularly in previously anaerobic soils, where oxidation rates are maximized. However, under field conditions, after a short-lived rise in C oxidation, rates decline again due to the formation of metal-organic complexes, which restrict the availability of DOC for microbial respiration. Our results suggest that these seasonally shifting controls on C oxidation rates across the floodplain are critical controls on C and metal export from the floodplain.

Export of metal-organic complexes varies depending on the hydrologic condition of the floodplain. We observe different metal-organic complexes, and the preference for metals of differing chemistry, depending on the metabolic conditions of the soil. Combining our biogeochemical measurements with hydrological investigations of the East River flood plain, we are developing a reactive transport modeling framework that examines carbon and metal transformations and export to river water. A multi-level well-field providing the capacity for determination of hydrologic gradients and pore-water chemistry is being utilized within two contrasting river meanders, representing end-members of hydrologic conductivity and oxygenation. Collectively, our results illustrate the combined, and dynamic, impacts of mineral- associations and metabolic controls on carbon and metal fate. The highly variable hydrology of floodplains leads to concomitant changes in biogeochemical processes within soils that ultimately control organic carbon, nutrients, and metal cycles.

Poster #22-18

Molecular and Genomic Insights into Nitrogen-Cycling Microbial Communities within the Terrestrial Subsurface at Riverton, WY

Christopher A. Francis^{1*}, Emily L. Cardarelli¹, Linta Reji¹, John R. Bargar², and Nicholas Bouskill³

¹ Stanford University, Stanford, CA

² SLAC National Accelerator Laboratory, Menlo Park, CA

³ Lawrence Berkeley National Laboratory, Berkeley, CA

Contact: caf@stanford.edu

BER Program: SBR

Project: University Award

Floodplains are hot spots for biological productivity that drive biogeochemical reactions and moderate ground and surface water quality, carbon turnover, and regional land-atmosphere interactions. Within the semi-arid upper Colorado River Basin (CRB) and intermountain west, a large fraction of shallow subsurface organic carbon (C) is believed to reside within fine-grained, organic-enriched sediments known as naturally-reduced zones (NRZs). NRZs, formed within the numerous contaminated DOE legacy site floodplains in the upper CRB, contain large inventories of nitrogen (N) and uranium (U). Microbial N-cycling has the capability to “unlock” the biogeochemical nutrient supply stored within NRZs, drive C cycling, and liberate U to the aquifers. Nitrification links organic matter decomposition to the production of nitrite and ultimately nitrate, an oxidant of U(IV) and the primary electron acceptor for denitrification. Nitrification and denitrification help mediate C turnover in NRZ sediments and are also the primary sources of the potent greenhouse gas, N₂O. Despite their biogeochemical importance, remarkably little is currently known regarding N-cycling microbial communities within terrestrial subsurface soils/sediments, let alone NRZs.

To address this critical knowledge gap, we are examining N-cycling communities at the DOE legacy U ore processing site in Riverton, WY, using a combination of molecular, meta-omic, biogeochemical, and modeling approaches. In addition to documenting the distribution and diversity of ammonia-oxidizing *Thaumarchaeota* using functional gene and high-throughput 16S rRNA amplicon analyses, we have recently obtained metagenome-assembled genomes (MAGs) from these biogeochemically-important *Archaea* from multiple depths within the Riverton subsurface. Ultimately, this multi-pronged approach will yield valuable genomic, ecophysiological, and biogeochemical insights into key microbial N-cycling guilds within the terrestrial subsurface.

Poster #21-11

On Dry Season Transpiration

Inez Fung^{1*}

¹ University of California, Berkeley, CA

Contact: ifung@berkeley.edu

BER Program: SBR

Project: University Award

Water is the principal regulator in biosphere-atmosphere interactions. High-frequency observations at a steep hillslope in the Mediterranean climate of northern California show that different proximate evergreen species have very different transpiration seasonality. A surprise is that Pacific Madrones show maximal daily transpiration in the dry summer season, with concomitant impacts on local energy and CO₂ exchange (Link et al. 2014). We hypothesize that the tree roots at the site have access to a deep store of water, as the water table some 20 meters below the surface exhibits very dynamic fluctuations with every rain storm. With DOE support, we have developed a stochastic parameterization of hydraulic conductivity that takes into account preferential flow through weathered bedrock (Vrettas and Fung, 2015), and applied the Richards Equation with the new parameterization to investigate the impact of subsurface water storage capacity (especially in the weathered bedrock) and rooting structure on the timing and magnitude of transpiration (Vrettas and Fung, 2017). The results show that it is the root mass below 4 meters that access the moisture in the weathered bedrock.

We have analyzed USDA Forestry Inventory and Analysis DataBase (FIADB) and mapped the spatial distribution of the 98 tree species in California. Our analysis shows tree mortality during the 2012-2016 drought does not map onto precipitation deficits for the period, but corresponds with differences in the root structure of the different species. We thus hypothesize that deep water stores accessible to deep roots are not unique to the research site, and could explain differential resilience to droughts and insect infestations across a landscape.

References:

Link, P., K. Simonin et al. (2014), Species differences in the seasonality of evergreen tree transpiration in a Mediterranean climate: Analysis of multiyear, half-hourly sap flow observations, *Water Resour. Res.*, 50(3), 1869–1894.

Vrettas, M. D., and I. Y. Fung (2015), Toward a new parameterization of hydraulic conductivity in climate models: Simulation of rapid groundwater fluctuations in Northern California, *J. Adv. Model. Earth Syst.*, 7(4), 2105–2135.

Vrettas, M. D., and I. Y. Fung (2017), Sensitivity of transpiration to subsurface properties: Exploration with a 1-D model, *J. Adv. Model. Earth Syst.*, 9(2), 1030–1045.

Poster #21-74

Physical, Resource Supply, and Biological Controls on Nutrient Processing Along the River Continuum

Ricardo González-Pinzón^{1*}, Jancoba Dorley¹, Kelli Feeser¹, and David J. Van Horn¹

¹ University of New Mexico, Albuquerque, NM

Contact: gonzaric@unm.edu

BER Program: SBR

Project: University Award

Excess nutrient loading has negatively impacted the ecology of ~90% of the streams in the US and the ecosystem services these streams provide, with estimated damages to US surface and groundwater system over of 100 billion dollar per year. Thus, there is a strong need to develop methods to predict the transport, uptake, and export of nutrients along fluvial networks and their cumulative effects on surface and groundwater quality. Our project is developing a data-driven, mechanistic understanding of critical 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 concentrations, stoichiometric constraints, etc.), and 3) biological controls (microbial community structure and function), and how these key factors drive nutrient uptake along a river continuum. This work is designed to address current knowledge gaps in understanding lotic nutrient dynamics that include a paucity of data for high order streams, a lack of studies assessing stoichiometric controls on nutrient uptake due to a traditional focus on solute-specific analyses (e.g., nitrogen only), and a scarcity of data that links microbial diversity and function with nutrient uptake dynamics along fluvial networks. Resolving these limitations will promote scientifically based restoration projects to reduce the burden of eutrophication costs. To meet our goals, we are pursuing three specific research objectives: RO1) Investigate how changes in river sediment texture control mass-transfer to metabolically active zones, colonizable surface area, and biological nutrient uptake along the river continuum; RO2) Investigate nutrient uptake kinetics along the river continuum considering limiting vs. non-limiting (i.e., stoichiometrically balanced) conditions, and labile vs. recalcitrant organic matter sources; and RO3) Investigate differences in microbial diversity, community structure, and genomic potential along the river continuum and how differences interact with resource supply to impose fundamental controls on nutrient uptake.

We are performing our research in a river continuum that spans four orders of magnitude in mean annual discharge (10^0 – 10^3 L/s), more than 2000 m in altitude, and more than 500 km of stream longitude. We incubated novel hollow-core columns filled with native and standardized sediments at each of the eight stream orders along the continuum for three months. The columns will be transported to the lab where tracer experiments will be performed under standardized flow conditions. Conducting the experiments with the two sediment types will provide the information necessary to determine how transport, normalized (by colonization and surface area) nutrient uptake rates, and variation in the biological community interact to influence nutrient uptake along the river continuum. Additionally, two resource supply injections will be performed on each of the columns: an only nitrate addition, followed by a stoichiometrically 'balanced' 106C:16N:1P addition. The stoichiometrically balanced injections will provide information necessary to determine how limitations for a given resource may impact nutrient uptake scaling in streams.

Our research seeks to depart from the status quo of focusing on solute-specific, site-specific nutrient uptake analyses, which have resulted in unscalable frameworks, to incorporate a more holistic, stoichiometrically and microbially based, data-driven mechanistic understanding of nutrient uptake and export along fluvial networks.

Poster #21-65

Water Management Impacts on Groundwater-River Water Exchanges

Abigail Conner^{1*}, Michael Gooseff¹, and Xingyuan Chen²

¹ INSTAAR University of Colorado, Boulder, CO

² Pacific Northwest National Laboratory, Richland, WA

Contact: abigail.conner@colorado.edu

BER Program: SBR

Project: University Award

Human activity along river corridors disturbs many critical river processes, including surface- groundwater exchanges. In many rivers, these exchanges provide important exchanges of energy, biota, and solutes between the surface and subsurface environments, and support fisheries and removal of some pollutants from rivers. This project aims to determine if water management activities within and beyond the river corridor impact groundwater exchanges. To determine this, we are studying the Hanford Reach of the Columbia River, in Southeast Washington. Since there are many challenges to using applied tracers in a large river system, this project aims to use natural tracers to determine locations of groundwater inflows, by taking water quality and GPS measurements along the streambed during boat surveys throughout the year. These measurements indicate the presence of groundwater inflows at the riverbed at several locations. We compare these inflows against locations of irrigation return flow and lateral contributing area to the exchange to identify the influence of each on river-groundwater exchange.

Several of these inflows show higher than main-channel levels of nitrate, suggesting impact from nearby shoreline irrigation. These insights will improve calibration models of hydrologic exchange developed by the River Corridor SFA at the reach scale of the Columbia River, as well as advance knowledge about the connection of landscape management to large river systems.

Poster #21-66

M&M: A Multi-Fidelity & Machine-Learning Approach to Model Hydrologic-Biogeochemical Processes in the Groundwater-Surface Water Interaction Zone

George Karniadakis^{1,2}, Xuhui Meng^{1*}, and Alexandre Tartakovsky²

¹ Brown University, Providence, RI

² Pacific Northwest National Laboratory, Richland, WA

Contact: george_karniadakis@brown.edu

BER Program: SBR

Project: University Award

We have developed a *multi-fidelity deep learning approach* suitable for optimal data acquisition, model discovery, model parameterization, and, ultimately, for predictive modeling of geo-physico-chemical processes for the Hanford site. Using a one-year exploratory grant we have developed a new multi-fidelity capability that has a tremendous potential for modeling hydrologic- biogeochemical processes in the groundwater-surface water interaction zone. We presented these results to SFA leader Dr. T. Scheibe and his team (January 23, 2019). We started with Gaussian Process Regression but we switched to deep neural networks (DNN) for easier training and scalability. We have designed a new architecture of a multi-fidelity physics-informed neural network (PINN) and obtained some results for solving the equation for unsaturated flows for the pressure height h . We assumed that we have *only two experimental measurements* and that we have several points from the FPLOTRAN simulation, which may not be very accurate. By using the multi-fidelity PINN we are able to obtain the correct solution and discover the correct hydraulic conductivity.

Poster #21-4

Root Influences on Mobilization and Export of Mineral-bound Soil Organic Matter

Marco Keiluweit^{1*}, Mariela Garcia-Arredondo¹, Zoe Cardon², Malak Tfaily³, Rosey Chu⁴, Rene Boiteau⁵, Steve Yabusaki⁴, and Yilin Fang⁴

¹ University of Massachusetts, Amherst, Amherst, MA

² Marine Biology Laboratory, Woods Hole, MA

³ University of Arizona, Tucson, AZ

⁴ Pacific Northwest National Laboratory, Richland, WA

⁵ Oregon State University, Corvallis, OR

Contact: keiluweit@umass.edu

BER Program: SBR

Project: University Award

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 goal of this project is to identify the (bio)geochemical mechanisms by which roots destabilize mineral-OM associations and the cumulative impact of OM mobilization on the fate of carbon and nitrogen. To accomplish this goal, we initiated model system experiments to assess the vulnerability of isotopically labeled OM bound to different soil minerals to various root-driven mobilization strategies. Our results show that OM bound to mineral phases with the greatest sorptive capacity are also the most susceptible to root-driven mobilization. We further highlight ongoing greenhouse experiments, as well as field-based experiments aiming to quantify the impact of root-driven OM mobilization across a hillslope transect in the subalpine East River watershed.

In addition, we have developed a well-controlled “rhizobox” approach to identify the (bio)geochemical mechanisms roots employ to mobilize OM from minerals. Using a combination of spatially-resolved micro(bio)sensors and high-resolution mass spectrometry, our results show how growing roots of *Festuca thurberi*, an abundant grass species across the East River watershed, alter the composition and availability of OM on extremely short time scale. Our data show that OM mobilization in the rhizosphere is linked to root growth, which promotes diurnal changes in redox and pH that control metal precipitation/dissolution. By parameterizing a rhizosphere (hydro)biogeochemistry reactive transport model, we are able to show that such OM dynamics in the rhizosphere are directly related to rhizodeposition and water fluxes. In sum, our initial results validate the strong control plant roots exert on the stability of mineral-OM associations in the rhizosphere and, thus, on the potential for C and N export from watersheds.

Poster #21-5

Distinct Source Water Chemistry Shapes Contrasting Concentration – Discharge Patterns

Wei Zhi¹, Li Li^{1*}, Wenming Dong³, Wendy Brown⁴, Jason Kaye¹, Carl Steefel³, and Kenneth H. Williams^{3,4}

¹ Pennsylvania State University, State College, PA

³ Lawrence Berkeley National Laboratory, Berkeley, CA

⁴ Rocky Mountain Biological Laboratory, Crested Butte, CO

Contact: lili@engr.psu.edu

BER Program: SBR

Project: University Award

Contrasting concentration-discharge (C-Q) behaviors have been observed for the same solute in different watersheds and for different solutes in the same watershed. A unified mechanistic understanding however remains elusive. This work tests the hypothesis that seemingly disparate C-Q behaviors are driven by switching dominance of end-members contributing to streams and their concentration contrasts arising from subsurface spatial heterogeneity. We use data from Coal Creek, a high-elevation mountainous catchment in Colorado and a recently-developed watershed reactive transport model (BioRT-Flux-PIHM) to gain mechanistic understanding; Monte-Carlo simulation (500 cases) casts the results under broader conditions. Results show that the switching dominance in the stream between organic-rich soil water during spring melt and organic-poor groundwater under dry conditions leads to flushing patterns of dissolved organic carbon (DOC). Dilution occurs for geogenic species (e.g., Na, Ca, Mg) that are abundant in groundwater with reactive rocks at depth. Monte-Carlo simulations indicate that concentration differences between soil and groundwater as end members determine the slopes (*b*) of C-Q patterns with a general relationship

$$b = (\delta_b C_{ratio}) / (C_{ratio,1/2} + C_{ratio}) + b_{min}$$

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 occurs; chemostasis occurs in between. The *b* values of 11 solutes (DOC, dissolved phosphorus, NO_3^- , K, Si, Ca, Mg, Na, Al, Mn, Fe) from three watersheds (Coal Creek, Shale Hills, Plynlimon) follow this equation. This indicates potentially broad applications of this equation to quantify *b* values given end-member concentrations in watersheds of diverse climate, geology, and land cover conditions.

Poster #21-6

Regolith, Rock and Fluid Distributions at the Upper Colorado River Basin via a Multicomponent Seismic Imaging Approach

James St. Clair¹ and Lee Liberty^{1*}

¹ Boise State University, Boise, ID

Contact: lliberty@boisestate.edu

BER Program: SBR

Project: University Award

Surface geophysical measurements can link geologic, geomorphic and hydrologic processes. Characterizing subsurface properties at sufficient resolution, yet over a large enough spatial extent to make statistically relevant correlations between subsurface structure and surface observations (topographic attributes, vegetation, etc.), is currently not standard practice because ground-based geophysical campaigns are limited by acquisition rates. The seismic land streamer is a semi-autonomous vehicle-mounted acquisition system designed to pull geophone arrays and a seismic source to rapidly acquire large data volumes compared to traditional planted geophone surveys. Acquisition geometry is well suited for obtaining first arrivals to constrain p-wave velocities (V_p), Rayleigh waves to constrain shear-wave (V_s) velocities and reflections to map significant subsurface stratigraphy. Joint and/or independent analysis of these semi-independent data sources reduce uncertainties in data interpretation.

In October 2018, we conducted an exploratory seismic survey of the East River Watershed Function Science Focus Area, near Crested Butte, CO. Our survey goals were to map seismic bedrock, regolith and sediment properties and relate them to geomorphic and hydrologic processes. Bedrock in the watershed is composed of Mancos Shale and younger crystalline intrusions. Hillslopes are mantled with weathered bedrock, moraines, landslides and colluvium. The watershed is roughly divided into an upper and lower flood plain separated by a locally steeper stream gradient with bedrock exposures in the river. We acquired ~12 km of seismic data along roads with a 72-channel, 1.25m spaced streamer and an average shot spacing of 2.5m and an average acquisition rate of 3 km/day. We also obtained ~3km of planted geophone data with geophone and shot spacings between 2.5 and 5 meters and an acquisition rate of 0.5 km/day.

Preliminary V_p results show a sharp transition between regolith and bedrock along hillslopes suggesting a similarly abrupt change in porosity. V_p anisotropy in the Mancos Shale suggests geologic structure drives bedrock groundwater flow. We note changes in V_p and V_s with elevation and slope, reflecting contact metamorphism away from intrusive rocks and the influence of sediment transport on seismic velocity. We show that the Upper Flood Plain contains about 20 meters of alluvium compared to <10 meters in the Lower Flood Plain, reflecting slope-dependent variations sediment transport along the watershed. Reflection images suggest channel morphology is controlled, in part by geologic structure.

Poster #21-7

Soil Respiration Across Scales

Kate Maher^{1*}, Matthew J. Winnick^{1,2}, Hsiao-Tieh Hsu¹, Yuchen Liu³, Jennifer L. Druhan³, and Corey R. Lawrence⁴

¹ Stanford University, Stanford, CA

² University of Massachusetts Amherst, Amherst, MA

³ University of Illinois at Urbana-Champaign, Urbana, IL

⁴ U.S. Geological Survey, Denver, CO

Contact: kmaher@stanford.edu

BER Program: SBR

Project: University Award

Soil respiration fluxes play a fundamental role in the terrestrial carbon cycle. Nevertheless, representing the processes that drive soil respiration in models remains an outstanding challenge due to an array of spatially- and temporally-dependent sensitivities to environmental drivers. In particular, the interactions between these drivers, such as plant phenology, temperature, and soil moisture remain largely uncharacterized. Another outstanding challenge is in partitioning between the heterotrophic and autotrophic components of respiration. To address these challenges, we have conducted incubation studies of soil respiration, characterized soil carbon stocks using spectroscopy and radiocarbon, and measured soil respiration rates in a subalpine meadow within the East River watershed, Gothic, CO over the 2016, 2017, and 2018 growing seasons. Laboratory incubations studies with variable soil moisture were used to test a moisture-dependent model framework for microbial respiration that captures the transition between dormant and active states. When the model is run using field measurements of soil moisture and soil carbon, the model successfully matches deep late season CO₂ profiles. To further constrain the parameters of this modeling framework, we are now extracting RNA/DNA ratios as a function of time to monitor the timescale of transition between active and dormant states. To quantify total soil respiration and understand how microbial processes translate to plot-scale measurements, we quantified depth- resolved net CO₂ production rates using observations of soil pCO₂ and surface efflux rates to drive a 1-D diffusion-reaction model. These rates were then compared to sensor monitoring data of soil moisture and temperature and to the MODIS satellite-derived enhanced vegetation index (EVI) as a proxy of plant phenology. A comparison of MODIS EVI across the field site between years demonstrated that when rain events occurred late in the growing season, as vegetation is senescing, soil respiration is significantly less responsive to increased soil moisture. Future work will examine the extent to which the plant response is further mediating the microbial response, potentially due to a reduction in exudate input. We also observe significant fluxes of CO₂ from the deep subsurface (> 165 cm) in the late growing season that likely persist under snowpack. Collectively, our results suggest that (1) plant phenology regulates the response of soil respiration rates to pulse wetting events and (2) deep subsurface carbon fluxes may constitute a significant portion of integrated annual surface CO₂ fluxes. Both processes will need to be adequately reflected on model representations to fully capture the response of ecosystems to a more variable water cycle.

Poster #21-8

Measuring the Link Between Energy and Water: Latent Heat Flux in Heterogeneous Mountain Environments

Anna Ryken¹, Dave Gochis², Ken Williams³, and Reed Maxwell^{1*}

¹ Colorado School of Mines, Hydrologic Sciences and Engineering, Golden, CO

² National Center for Atmospheric Research, Boulder, CO

³ Lawrence Berkeley National Laboratory, Berkeley, CA

Contact: rmaxwell@mines.edu

BER Program: SBR

Project: University Award

Snowpack in high elevation regions of the Colorado River basin contributes to seventy percent of the Colorado River streamflow, which provides water to thirty million people. Despite the importance of these regions for downstream water delivery, water availability from these mountain sources is vulnerable to the changing climate. However, the effect of climate change on these regions is difficult to characterize given Earth System Models' poor representation of high-elevation, mountainous regions. These regions are difficult to represent in large-scale models due to their large topographic gradients, heterogeneous land cover, and complex atmospheric patterns. Our DOE SBR Exploratory Project has combined observations and models to better characterize water, energy and CO₂ fluxes in a headwaters system. A combination of point observations and high-resolution models are used to estimate these hydrologic fluxes in a Colorado River headwaters region, near Crested Butte, Colorado. Using data from an eddy flux tower collocated with a metrological station in the East River basin, this study has collected almost two years of observations that include latent and sensible heat fluxes. Initial observations are consistent with expected results and within reasonable bounds; latent heat is greatest in the spring as vegetation begins growing and lowest in the winter due to snow cover. Conversely, sensible heat peaks before total snow melt and decreases as latent heat increases. These initial results show promise for accurately modeling energy fluxes and plant water use in this heterogeneous mountain region.

Poster #21-52

Influence of Redox Reactions and Organic Ligand Complexation on Uranium, Neptunium, Technetium Subsurface Transport: Upscaling Laboratory Experiments to Understand Field Lysimeter Data

Brian A. Powell^{1,2*}, Timothy A. DeVol¹, Stephen Moysey¹, Lawrence Murdoch¹, Mine Dogan¹, Nimisha Edayilam¹, Brennan Ferguson¹, Jeffrey Hundley¹, Daniel I. Kaplan^{1,2}, Abdullah Al Mamun¹, Melody Maloubier¹, Nicole Martinez¹, Dawn Montgomery¹, Kathryn Peruski¹, and Nishanth Tharayil¹

¹ Clemson University, Clemson, SC

² Savannah River National Laboratory, Aiken, SC

Contact: bpowell@clemson.edu

BER Program: SBR

Project: University Award

Project Website: <https://www.clemson.edu/centers-institutes/neesrwm/EPSCoR>

The migration of trace elements in the environment is dependent on the chemical species which dominate under given geochemical conditions. The mobility can be enhanced or retarded by altering the oxidation state or forming soluble organic ligand-metal ion complexes. This work examines three case studies to evaluate the impacts of these changes in chemical speciation on the transport of trace elements through soil. Our approach seeks to characterize the time and length scales over which non-equilibrium states are maintained by rate-limiting (or rate-enhancing) reactions between radionuclides and co-reactants due to interactions between physical mass-transfer processes (i.e., flow, advection, diffusion) and (biogeo)chemical reactions.

Neptunium and technetium transport in field lysimeter studies has demonstrated enhanced mobilization of Np and Tc due to oxidation of Np(IV) to Np(V) and Tc(IV) to Tc(VII). Solid NpO₂(s) and Tc amended cementitious waste form samples were deployed in field lysimeters for up to 2 years. The effluent concentrations of Np and Tc were continually monitored and after retrieval from the field, the lysimeters were destructively sampled to determine the solid phase concentrations of Np and Tc as a function of depth in the lysimeter. The retrieved solid phases indicated surficial oxidation of NpO₂(s) along grain boundaries and leaching of Tc from corrosion rinds of the cementitious waste form. Both processes are controlled by redox gradients between the soil pore water and the waste forms. Complimentary laboratory testing has evaluated the rate and extent of source term oxidation and demonstrated that strong reducing gradients downgradient of the source can reduce Tc(VII) to immobile and insoluble Tc(IV). These measurements are enabled by the development of real-time, in-situ radioisotope monitoring techniques by our team.

A second mechanism by which the mobility of ions can be altered is through complexation with organic ligands. This work has examined the influence of nutrient availability, plant roots and plant root exudates on preferential water flow through field lysimeters and dissolution of uranyl phosphate minerals through formation of soluble U(VI)-ligand complexes. Results indicate that less soluble phosphate sources lead to enhanced plant exudate production which in turn enhances uranium solubility and mobility. These results were verified using flow-through batch reactor experiments examining the dissolution of uranyl phosphate by citric acid (a common phytosiderophore). Ongoing field lysimeter experiments with and without plants are examining these processes on larger spatial and temporal scales.

This material is based upon work supported by the U.S. Department of Energy Office of Science, Office of Basic Energy Sciences and Office of Biological and Environmental Research under Award Number DE-SC-00012530.

Poster #21-2

Investigating Bedrock Fractures as a Dynamic Hydrologic Reservoir Across a Gradient in Climate and Erosion Rate

Daniella Rempe^{1*}, Logan Schmidt¹, Mong-han Huang², Kristen Fauria³, Jennifer Druhan⁴, W. Jesse Hahm⁵, William E. Dietrich⁵, and David Dralle⁶

¹ University of Texas at Austin, Austin, TX

² University of Maryland, College Park, MD

³ Woods Hole Oceanographic Institute, Woods Hole, MA

⁴ University of Illinois, Urbana Champaign, Champaign, IL

⁵ University of California, Berkeley, Berkeley, CA

⁶ Sacramento State University, Sacramento, CA

Contact: rempe@jsg.utexas.edu

BER Program: SBR

Project: University Award

The weathered and fractured bedrock that commonly underlies soils in montane environments can be sufficiently porous and permeable to transiently store and transmit water. There is increasing inferential evidence that this variably saturated weathered bedrock region regulates subsurface biogeochemical processes and the partitioning of precipitation between evapotranspiration and runoff. However, observations of hydrologic dynamics in the bedrock unsaturated zone are sparse, and thus the representation of this region in models of land-surface processes remains poorly constrained. This project seeks to evaluate predictions of how the weathering profile is structured at the hillslope scale by assembling direct observations within four sites underlain by clay-rich bedrock (i.e. shale) across a gradient in climate and erosion rates: the Angelo Coast Range Reserve (ACRR), Sagehorn-Russell Ranch (SRR), Antelope Valley Ranch (AVR), and the LBNL Watershed Function Scientific Focus Area (SFA). To complement existing boreholes at ACRR and SRR, we have now established field monitoring sites in forested shale bedrock at the AVR and SFA sites. The boreholes were outfitted with pressure transducers to monitor groundwater levels and we are currently characterizing mineralogy, geochemistry and pore structure on cores.

With the establishment of new boreholes, we have now documented significant water storage in weathered bedrock using low-field borehole nuclear magnetic resonance (NMR) across all four sites. In the upper 4 m of bedrock, the average water contents at ACRR, AVR, SRR, and SFA are approximately 25%, 16%, 25%, 23% respectively. At the ACRR site, where long-term monitoring via neutron probe surveys and time-domain transmission sensors are available, we have demonstrated that NMR reliably records moisture content and importantly, moisture content dynamics in weathered bedrock. Across all sites, our NMR monitoring has also revealed that a considerable fraction of the water storage occurs in fractures or pores that are significantly larger than the fine-grained bedrock matrix of the parent rock. To identify the proportion of water storage occurring in fractures and large pores, we analyzed the NMR signal by evaluating both the sum of echoes and an inversion of the NMR signal for a distribution of T_2 relaxation times. Both methods reveal that at least 20% of the water storage occurs in fractures and larger pores across all sites. To constrain the interpretation of the in-situ field-scale NMR measurements, we are comparing the NMR response of variably saturated core samples to independent pore-structure information obtained via pycnometry and micro-CT. Preliminary results support the inference that dynamic seasonal water storage is dominantly restricted to the fracture network, which can reach 7% of the total volume. This dynamic range in water content is comparable to that of some soils, underscoring the need to understand how this region of the Earth System is structured, and functions as a hydrologic reservoir.

Influence of Hyporheic Exchange on Coupled S-Fe-C Biogeochemical Cycling in Riparian Wetland Sediments

Cara M. Santelli^{1*}, Crystal Ng¹, Aubrey Dunshee¹, Carla Rosenfeld^{1,2}, Daniel Kaplan³, Kenneth Kemner⁴, Edward O'Loughlin⁴, Pamela Weisenhorn⁴, and Maxim Boyanov⁵

¹ University of Minnesota, Minneapolis, MN

² Northwestern University, Evanston, IL

³ Savannah River National Laboratory, Aiken, SC

⁴ Argonne National Laboratory, Argonne, IL

⁵ Bulgarian Academy of Sciences, Sofia, Bulgaria

Contact: santelli@umn.edu

BER Program: SBR

Project: University Award

Riparian wetland hyporheic zones, where oxic surface water and anoxic groundwater mix, exhibit dynamic conditions that drive steep redox gradients and promote hotspots and hot-moments of diverse and fluctuating microbial activity. There is growing evidence that highly active “cryptic” sulfur cycling processes drive the fate of iron and carbon and respond to dynamic hyporheic fluxes in riparian wetlands. These “hidden” or “cryptic” sulfur redox processes are not well constrained in freshwater systems but can include the production of reactive intermediate S species that promote further biotic and abiotic redox reactions (including those coupled with Fe reduction and methane oxidation), thus supporting higher rates of sulfur biogeochemical cycling than otherwise expected in these low sulfate environments. The overall goal of this project is to develop a mechanistic understanding of how hydrologic flow influences coupled abiotic-biotic Fe-S- methane cycles in riparian wetlands. Our specific objectives are to (1) measure the fate and transport of Fe, S, and CH₄ in dynamic riparian wetlands, (2) evaluate the microbial community structure and potential function driving these cycles, (3) incorporate “cryptic” S-Fe-C processes into a reactive transport model to examine hyporheic flux impacts, and (4) assess how increased sulfate loading can alter coupled S-Fe-C processes. We will present preliminary results of our geochemical analyses (Fe and S speciation and abundance in sediments, porewaters, and surface waters) and hydrologic flux measurements in an organic-rich riparian wetland at Tims Branch, part of the Argonne Wetland Hydrobiogeochemistry SFA. We will compare these results to findings at a riparian wetland site in northern Minnesota with higher surface water sulfate loading, for which we have implemented a reactive transport model that has provided evidence for these cryptic sulfur redox processes.

Poster #21-51

Natural Organic Matter and Microbial Controls on Mobilization/Immobilization of I and Pu in Soils and Waters Affected by Radionuclide Releases in USA and Japan.

Peter H. Santschi^{1*}, Chen Xu¹, Peng Lin¹, Kathleen A. Schwehr¹, Daniel I. Kaplan², Chris M. Yeager³, and Patrick G. Hatcher⁴

¹ Texas A&M University at Galveston, Galveston, TX

² Savannah River National Laboratory, Aiken, SC

³ Los Alamos National Laboratory, Los Alamos, NM

⁴ Old Dominion University, Norfolk, VA

Contact: santschi@tamug.edu

BER Program: SBR

Project: University Award

Examining the short-term deposition and forecasting the long-term fate of plutonium (Pu) is becoming increasingly important as more worldwide military and nuclear-power waste is being generated. Soils from the Fukushima Prefecture provided the opportunity to compare Pu from reactor fallout in the litter layer to that derived from 1960's bomb fallout in the underlying soil. Additionally, we used this unique opportunity to explore the long-term behavior of Pu in Nagasaki sediments, where bomb-derived Pu was deposited in 1945. A combination of selective extractions and molecular characterization via electrospray ionization Fourier-transform ion cyclotron resonance mass spectrometry (ESI-FTICRMS) were used in an attempt to resolve what regulated the long-term stabilization of $^{239,240}\text{Pu}$ in Nagasaki bomb residue-containing sediments (>400 cm) and the short-term deposition of nuclear plant accident-derived $^{239,240}\text{Pu}$ in Fukushima Prefecture (<12 cm). In deep Nagasaki sediments, our results demonstrated that $55\pm 3\%$ of the $^{239,240}\text{Pu}$ was preferentially associated with more persistent organic matter compounds, particularly those natural organic matter (NOM) stabilized by Fe oxides ($\text{NOM}_{\text{Fe-oxide}}$). Other organic matter compounds served as the secondary sink of these bomb-derived $^{239,240}\text{Pu}$ ($31\pm 2\%$ on average), and less than 20% of the bomb-derived $^{239,240}\text{Pu}$ was immobilized by the inorganic mineral particles. In a 9-cm thick, $^{239,240}\text{Pu}$ -enriched layer at ~400cm depth, N-containing carboxyl aliphatic and/or alicyclic molecules (CCAM) in $\text{NOM}_{\text{Fe-oxide}}$ and other NOM fractions immobilized the majority of $^{239,240}\text{Pu}$. Among the cluster of N-containing CCAM moieties, hydroxamate siderophores, the strongest known Pu chelators in nature, were further detected in these "aged" Nagasaki bomb residue-containing sediments. In Fukushima Prefecture and Nagasaki sediments, the NOM still served as the predominant sink for these nuclear plant accident-derived $^{239,240}\text{Pu}$ (sum of $\text{NOM}_{\text{Fe-oxide}}$ and other organic matter). While present long-term disposal and environmental remediation modeling assume that solubility limits and sorption to mineral surfaces control Pu subsurface mobility, our observations suggest that NOM, which is present in essentially all environmental systems, undoubtedly plays an important role in sequestering Pu. Ignoring the role of NOM in controlling Pu fate and transport is not justified in most environmental systems*.

References:

* Lin, P., Xu, C., Kaplan, D.I., Chen, H.M., Sun, L., Yeager, C.M., Xing, W., Sun, L., Schwehr, K.A., Yamazaki, H., Saito-Kokubu, Y., Hatcher, P.G., Santschi, P.H. 2018. Nagasaki sediments reveal that long-term fate of plutonium is controlled by select organic matter moieties. STOTEN, submitted.

Poster #22-3

Constraining Physical Understanding of Aerosol Loading, Biogeochemistry, and Snowmelt Hydrology from Hillslope to Watershed Scale in the East River Scientific Focus Area

R. McKenzie Skiles^{1*}, David Gochis², Janice Brahny³, Hannah Peterson¹, and Joachim Meyer¹

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

BER Program: SBR

Project: University Award

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.

Multiscale Modeling of Mercury Geochemistry

Jeremy C. Smith^{1,2*}, Scott C. Brooks², Peng Lian¹, Deepa Devarajan¹, Luanjing Guo¹, Scott L. Painter², and Jerry M. Parks²

¹ University of Tennessee Knoxville, Knoxville, TN

² Oak Ridge National Laboratory, Oak Ridge, TN

Contact: smithjc@ornl.gov

BER Program: SBR

Project: University Award

Project Website: <https://aquamer.ornl.gov>

In natural aquatic environments, the transport of mercury (Hg) inorganic and organic complexes takes place in flowing water and simultaneously with equilibrium and kinetic reactions. A web-based multiscale modeling aqueous speciation resource (*AQUA-MER*) has been developed for the aqueous biogeochemical speciation of metals in environment. *AQUA-MER* integrates the calculation of atomistic first-principles based thermodynamic constant with continuum-scale speciation modelling for metals. In general, the continuum-scale speciation calculations use thermodynamic stability constants ($\log K$) to predict the mesoscale distribution of Hg. However, experimental $\log K$ values are not available for many relevant complexes and for others can span ranges in excess of 10 log units. We investigated the effects of $\log K$ uncertainties on speciation calculations. We showed that thermodynamic parameter uncertainties can lead to output concentrations spanning several orders of magnitude and by performing the uncertainty analysis we could identify environmental regimes where uncertainty is important to consider in speciation modeling. Accurate and reliable quantum chemical approaches have been developed and implemented in *AQUA-MER* for the $\log K$ calculation of Hg complexation with inorganic and low-molecular weight organic compounds. High molecular weight dissolved organic matter (DOM) in the natural environment can also bind with Hg, forming stable complexes. However, the experimental $\log K$ values vary between ~ 31 and 42 log units for $\text{Hg}(\text{DOM})_2$ because of the difficulties in the molecular level characterization of the highly heterogeneous DOM. Atomistic MD simulation can capture the details of aggregation and distribution of functional groups in DOM at the molecular level. 100 ns time scale molecular dynamics simulations reveal the initial aggregation of various components of DOM forming complex structures. At the continuum-scale, a travel-time based reactive transport model in the hyporheic zone of stream corridors was established for the multicomponent Hg-DOM-S system and implemented through PFLOTRAN. Sulfur redox zonation was accounted for using a prescribed oxygen gradient. Temporal and spatial distributions of Hg-containing species along the vertical axis of a single sediment bedform were obtained and analyzed. Future studies will focus on integrating the Hg-DOM complexation mechanisms obtained from atomistic MD simulations into continuum-scale reactive transport simulations. We present an information-theoretic approach that allows for seamless integration of multi-resolution data into multi-scale simulations to upscale/downscale hydraulic conductivity of heterogeneous porous formations. Available data (at either the fine- or the coarse-scale) are used to inform models at the opposite scale by setting a probabilistic equivalence between the fine and the coarse scale, with closures (parameters and/or constitutive laws) that are learnt via minimization of observables error and mutual information across scales. We investigate how this can guide us to formulate scaling laws and we explore means to accelerate scaling of dynamic processes and to reduce data requirements.

Poster #21-24

Assimilation of Multiscale Data into Multifidelity Biogeochemical Models

Daniel M. Tartakovsky^{1*} and Ilya Timofeev²

¹ Stanford University, Stanford, CA

² University of Houston, Houston, TX

Contact: tartakovsky@stanford.edu

BER Program: SBR

Project: University Award

Vast disparity of spatiotemporal scales on which data are collected and models are used remains one of the key challenges in accurate and reliable predictions of watershed dynamics. We generate multi-resolution data by developing novel regression- and neural network-based closures for averaged (watershed-scale) equations of flow and transport. Then, we introduce an information-theoretic approach that allows for seamless integration of multi-resolution data into multi-scale simulations to upscale/downscale hydraulic conductivity of heterogeneous porous formations. Available data (at either the fine- or the coarse-scale) are used to inform models at the opposite scale by setting a probabilistic equivalence between the fine and the coarse scale, with closures (parameters and/or constitutive laws) that are learnt via minimization of observables error and mutual information across scales. We investigate how this can guide us to formulate scaling laws and we explore means to accelerate scaling of dynamic processes and to reduce data requirements.

Poster #22-16

Influx of Oxidants into Reduced Zones: Microbiological Controls Governing Metal Oxidation and Reduction

Karrie A. Weber^{1*}, Rebecca Lai¹, Josh Herr¹, John Bargar², and Romy Chakraborty³

¹ University of Nebraska—Lincoln, Lincoln, NE

² SLAC, Stanford, CA

³ Lawrence Berkeley National Laboratory, Berkeley, CA

Contact: kweber@unl.edu

BER Program: SBR

Project: University Award

Subsurface sediments are heterogeneous due to burial of soil horizons and organic matter. The high concentration of sediment-associated organic matter generates zones that are “biogeochemical hotspots”. These organic-rich deposits are recognized to drive metal/radionuclide reduction and trap reduced chemical species (i.e. (Fe(II)) including contaminants such as uranium (U(IV)). Thus reduced regions play a significant role trapping contaminants preventing mobility in groundwater. The existing paradigm describes oxidation of reduced metals/radionuclides upon the influx of dissolved oxygen and/or nitrate into reduced zones. However in contrast to the existing paradigm results from prior field and laboratory results demonstrated that low concentrations of oxidants directly injected into a reduced aquifer sediments stimulated reduced conditions and a decrease in groundwater uranium concentrations. We hypothesize that the influx of low oxidant concentrations into reduced zones results in the production of dissolved organic carbon (DOC) as a result of organic carbon decomposition and/or stimulation of microbial/viral activity. Whereby, the production of DOC drives reducing conditions leading to further metal/radionuclide reduction (U immobilization). However, elevated concentrations of oxidants above a “tipping point” will drive net metal/radionuclide oxidation, resulting in an increase in aqueous U concentrations. Here a series of bioreactor based experiments amended with naturally reduced organic-rich sediment from Riverton, WY are amended with U. Experiments are ongoing to monitor carbon, iron, and uranium geochemistry as well as the microbial community. This research will identify and describe the phenomena related to oxidation and reduction of metals/radionuclides in reduced regions of aquifers upon the influx of oxidants such as dissolved oxygen and/or nitrate.

Poster #22-15

Complex Effects of Redox Reactions on the Release and Degradation of Organic Carbon

Yu Yang^{1*}, Eric E. Roden², Daniel Obrist^{3,4}, Annie B. Kersting⁵, and Baohua Gu⁶

¹ University of Nevada, Reno

² University of Wisconsin, Madison

³ Desert Research Institute

⁴ University of Massachusetts, Lowell

⁵ Lawrence Livermore National Laboratory

⁶ Oak Ridge National Laboratory

Contact: yuy@unr.edu

BER Program: SBR

Project: University Award

Recent studies have suggested the potential for the release of iron (Fe) oxides-bound organic carbon (OC) during dissimilatory Fe reduction (DIR). However, the extent to which different forms of Fe oxide-bound (e.g. sorbed vs. co-precipitated) OC are released during DIR has not been fully resolved. Pure ferrihydrite (Fh) and Fh-humic acid coprecipitates (Fh-HA) were inoculated with a small quantity of freshwater sediment and incubated under anoxic conditions in the presence and absence of H₂ or glucose as electron donors for DIR. Our results indicate that DIR can release loosely bound (e.g. sorbed) OC but may not from Fe oxide-OC coprecipitates.

Applying Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS), we investigated the fractionation of dissolved organic carbon (DOC) during co-precipitation with Fh in systems with C/Fe molar ratio of 0.5 and 3. Our results showed that high-molecular-weight DOC was preferentially precipitated for system with C/Fe of 3. In addition, a higher fraction of condensed polycyclic aromatic hydrocarbons (98.12%) was co-precipitated compared to unsaturated phenolic (66.25%) and aliphatic (39.01%) DOC. Our findings demonstrated that high-molecular-weight aromatic compounds preferentially co-precipitate with Fh in systems with feed C/F ratio relevant to the natural systems.

In the field, year-round measurements of ecosystem-scale methane and carbon dioxide fluxes were undertaken at Toolik Field Station in the Alaskan Arctic over two years. Year 1 cold season net carbon dioxide and methane fluxes, however, were 47 % and 150 % higher, over a shorter cold season (22 days shorter). Relationships between methane fluxes and surface temperatures were almost reversed to Year 2, though similar relationships between respiration fluxes and surface soil temperature were observed across both years. Our results suggest that high cold season methane emissions are linked to temperature thresholds in deep, active layer zones and highlight a need for measurement and modelling of soil temperatures throughout the year and entire active profile in order to better predict potential changes in the annual methane exchange budget in Arctic tundra regions.

Poster #21-23**Using Global Sensitivity Analysis to Identify Controlling Processes of Complex Systems**Ming Ye^{1*}, Gary Curtis², and Li Li³¹ Florida State University, Tallahassee, FL² U.S. Geological Survey, Menlo Park, CA³ Pennsylvania State University, State College, PAContact: mye@fsu.edu

BER Program: SBR

Project: University Award

For an open and complex environmental system, it is always difficult, if not impossible, to understand all the processes and their interactions. On the other hand, since the system dynamics are determined mainly by controlling processes, a better understanding of the controlling processes can lead to advanced predictive understanding of the system. Therefore, identifying controlling processes is always the first step for gaining predictive understanding. The identification, however, is challenging because of uncertainty inherent in system processes such as process parameters and conceptualizations. 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?* To answer this question, this project introduces the concept of multiple working hypotheses into the identification of controlling processes to explicitly take into account the uncertainty in conceptualizing and simulating individual processes.

In this poster presentation, we will first present a case study that uses sensitivity analysis to improve a nitrogen transport model developed based on the mixing layer theory. The sensitivity analysis considers three parameters, the mixing layer thickness and two mass transfer coefficients from the mixing layer, and identifies that the mixing layer thickness is the most important parameter. In other words, the nitrogen mixing process is more important than the mass transfer process. To improve the nitrogen transport model, a time-dependent equation is derived to estimate the mixing layer thickness to replace the constant mixing layer thickness used in the conventional mixing layer theory. Using the time-dependent mixing layer thickness substantially improves the model fit to observed nitrogen concentrations in a laboratory experiment.

Another achievement made in this project is the improved computational efficiency for calculating the process sensitivity index, which is the key variable for identifying dominating processes. The calculation is based on Monte Carlo simulation, and the original way of calculation is computationally expensive because it is based on combinations of model parameter samples. We developed a new method to remove the sample combination, which reduces the number of model simulation from the order of N^2 to N , N being the number of parameter samples. We are implementing the new computational method for uranium reactive transport modeling at Naturita, which involves three processes, i.e., groundwater flow, uranium transport, and uranium surface complexation reaction. The goal is to identify the controlling processes for contaminant remediation.