Elucidating Coupled Solute Transport, Transformation, and Ecosystem Processes in River Corridors using Stream Tracers

Marie Kurz[1]*, Scott C. Brooks[1], Scott Painter[1], Saubhagya Rathore[1], Adam Ward[2]

[1]Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN
[2]O'Neill School of Public and Environmental Affairs, Indian University, Bloomington, IN

(kurzmj@ornl.gov)

Project Lead Principal Investigator (PI): Eric M. Pierce

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Project Abstract: Metabolically active transient storage zones in stream ecosystems, most notably the hyporheic zone, are ecological and biogeochemical hotspots that exert control over geochemical and metabolic processing and regulate the distribution and transformation of matter and energy in river systems. Multiple natural and anthropogenic factors, including channel morphology, dynamic hydrology, and modifications to nutrient regimes, drive changes in the solute transport dynamics and reactivity of transient storage zones over time and space, which should, in turn, influence rates of whole-stream ecosystem functions such as metabolism and both assimilatory and dissimilatory nutrient transformations. However, there remains uncertainty about the coupling between solute transport, transient storage, and stream ecosystem function within streams, and the relative importance and organization of these coupled processes across systems and watershed scales. Additionally, we lack understanding about the relative importance and organization of these coupled processes across systems and watershed scales. Improving the representation of these coupled processes in both our conceptual and numerical models is essential to developing a more robust predictive understanding of functioning within river corridors. Here, we present insights gained from stream tracer experiments employed across a range of lotic systems to evaluate transient storage and aerobic respiration in relation to varied spatio-temporal patterns in stream structural controls and ecosystem processes. We also summarize new forward modeling capability and uncertainty-aware model-based interpretation approaches that leverage results from the stream tracer experiments. We identify challenges, opportunities, and new experimental approaches for expanding our process understanding across systems and scales and linking this understanding to reach-scale simulations of transport and transformation.

Understanding Environmental Controls on the Composition, Function, and Cycling of Mercury within Fluvial Periphyton

Spencer Washburn,[1] Scott C. Brooks,[1*] Grace E. Schwartz,[2] Scott Painter,[1] Saubhagya S. Rathore,[1] Alyssa A. Carrell,[3] Melissa A. Cregger,[3]

[1]Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN;
[2]Wofford College, Department of Chemistry, 429 N. Church St, Spartanburg, SC;
[3]Biosciences Division, Oak Ridge National Laboratory, Oak Ridge, TN;

(brookssc@ornl.gov)

Project Lead Principal Investigator (PI): Eric M. Pierce

BER Program: ESS

Project: Critical Interfaces Science Focus Area (Oak Ridge National Laboratory)

Project Website: https://www.esd.ornl.gov/programs/rsfa/

Project Abstract: Periphyton biofilms are complex assemblages that consist of algae, bacteria, fungi, detritus, extracellular polymers, invertebrates, and mineral particles. These complex biofilms play an integral role in stream ecohydrology as they are control points for ecosystem respiration, primary productivity, and organic matter cycling, while providing an important food source for higher trophic position organisms. Identifying the environmental physicochemical factors (e.g., disturbance regime, nutrient concentrations) that contribute to observed variability in fluvial biofilm community structure and function is needed for developing predictive models of stream biogeochemistry.

One poorly constrained biogeochemical function of fluvial biofilms is the production of monomethylmercury (MMHg) from inorganic mercury (Hg). Fluvial periphyton communities host the active anaerobic microbes capable of the microbially-catalyzed production of MMHg due to the steep geochemical gradients between fully oxic and anoxic conditions within these biofilms. Controlled laboratory experiments have demonstrated that actively photosynthesizing biofilms may generate a significant fraction of the MMHg flux in East Fork Poplar Creek (EFPC), a Hg contaminated creek in Oak Ridge, TN.

To better understand the relationship between environmental physicochemical factors and periphyton biofilm composition and function, we are conducting in-stream experiments within EFPC across multiple seasons to control for temporal variability. Utilizing a natural gradient of nutrient concentrations between two locations within EFPC, we can determine functional characteristics of biofilm colonized under relatively lower and higher nutrient concentrations, as well as assess the impacts of altering the nutrient regime to which an established periphyton community is exposed via physical translocation between locations. The resulting biofilms are then used in experiments to quantify measures of function (Hg methylation and MMHg demethylation kinetics, production of thiol-containing biomolecules) and community composition

(16s, 18s, ITS, and *hgcA* sequencing). Application of our transient availability model, developed for quantifying Hg methylation kinetics in biofilms, to biofilms grown under experimental treatments of varying length will allow us to quantify the impact of seasonally variable physicochemical factors on periphyton methylation rates. Sequencing data will be utilized to evaluate the relative impacts of community structure and interaction within the periphyton microbiome that drive variations in observed rates of Hg transformation. By providing insights into the environmental controls on the community composition and function of complex fluvial biofilms, this work aims to inform future research into the critical ecosystem processes in river corridors impacted by the activity of periphyton assemblages.

Linking Trace Metal Biogeochemistry and Carbon-Nutrient Cycling: The Role of Metallophores

Alexander Johs[1*], Baohua Gu[1], Xujun Liang[1], Peter Eckert[1], Lijie Zhang[1], Christina S. Kang[1], Jocelyn Richardson[2], Ritimukta Sarangi[2], Alan A. DiSpirito[3], Jeremy D. Semrau[4], Scott C. Brooks[1], Eric M. Pierce[1]

[1]Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN;
[2]Structural Molecular Biology Division, SLAC National Accelerator Laboratory, Menlo Park, CA;
[3]Department of Biochemistry, Biophysics and Molecular Biology, Iowa State University, Ames, IA;
[4]Department of Civil and Environmental Engineering, University of Michigan, Ann Arbor, MI

(johsa@ornl.gov)

Project Lead Principal Investigator (PI): Eric M. Pierce

BER Program: ESS

Project: Critical Interfaces Science Focus Area (Oak Ridge National Laboratory)

Project Website: https://www.esd.ornl.gov/programs/rsfa/

Project Abstract: Metal ions are essential components of metalloenzymes, which drive many biogeochemical carbon and nutrient cycles at the molecular scale. Microorganisms have developed strategies to overcome potential trace metal limitations by utilizing metallophores to facilitate the efficient uptake of trace metals. Thus, metallophores assume a significant role in controlling the bioavailability of trace metals. Metalloenzymes catalyze many key reactions driving critical metabolic processes, and they work at the interface between the cycling of trace metals and macronutrients, such as carbon and nitrogen. Methanobactin, a small peptide produced by some methanotrophs, is an example of a metallophore involved in copper (Cu) acquisition by methanotrophic bacteria linking the trace metal copper to the cycling of carbon (methane) in the environment. Additionally, methanobactins are known to form strong complexes with other transition metals, such as Hg, Zn, and Cd, affecting their biogeochemical transformations and bioavailability.

In this work, we present several case studies, such as discoveries of two novel methanotroph strains, *Methylomomas* sp. strain EFPC1 and *Methylococcus* sp. strain EFPC2, isolated from East Fork Poplar Creek, a Hg-contaminated stream in Oak Ridge, Tennessee, and interspecies interactions among methanotrophs. We show that some methanotrophs lacking genes for methanobactin biosynthesis are not limited for Cu by utilizing methanobactins produced by others. Certain methanobactins are also found to enhance the rate and efficiency of Hg methylation by the mercury-methylating bacteria, *D. desulfuricans* ND132 and *G. sulfurreducens* PCA, due to the formation of Hg-methanobactin complexes. We also investigate the interplay between solution-phase configurations, metal interactions and the spectroscopic signatures of methanobactin-metal complexes. Our results represent the first combined computational and experimental spectroscopy study of methanobactins and shed new light on molecular interactions and dynamics that

characterize complexes of methanobactins with Group 12 transition metals. Collectively our results underscore the complex roles of exogenous metallophores produced by microbes in controlling bioavailability and biogeochemical transformation of metals, which in turn exert a modulating influence on carbon and nutrient cycling in the environment.

Effects of Coupled Biogeochemical Processes on Soil Organic Carbon Storge and Fluxes

Elizabeth Herndon,[1,2*] Fernanda Santos,[1] Benjamin Sulman,[1] Jessica Moore,[1] Sindhu Jagadamma,[2] Avishesh Neupane[2]

[1]Oak Ridge National Laboratory, Oak Ridge, Tennessee
[2]The University of Tennessee, Knoxville, Tennessee

(herndonem@ornl.gov)

Project Lead Principal Investigator (PI): Eric M. Pierce

BER Program: ESS

Project: Critical Interfaces Science Focus Area (Oak Ridge National Laboratory)

Project Website: https://www.esd.ornl.gov/programs/rsfa/

Project Abstract: Improved understanding of the biogeochemical processes that regulate decomposition of organic matter and their incorporation into process-based models are needed to predict how watersheds will store and process carbon (C) in response to changing climate. Current ecosystem representations focus largely on biological components and disregard geochemical processes; however, soil carbon storage and fluxes are regulated by complex biotic and abiotic interactions amongst organic matter, nutrients, and metals. The objective of this research is to use laboratory, field, and modeling experiments to investigate interactive effects of manganese (Mn), nitrogen (N), and warming on leaf litter decomposition and organo-mineral interactions. Dissolved Mn stimulates enzymatic oxidation of recalcitrant lignin by soil microorganisms and may serve as a limiting nutrient to decomposition. Furthermore, Mn enrichment has been proposed to counteract inhibitory effects of N deposition on decomposition rates.

In a field decomposition experiment, surface organic soils were enclosed in nylon mesh bags and incubated for up to one year in upland soils of the temperate forested Walker Branch watershed in east Tennessee. Soils were either warmed +2-3°C or not and received between zero to 10 mg g^{-1} monthly aqueous Mn(II) addition. Measurements of litter mass loss and soil respiration were coupled with spectroscopic measurements and microbial analyses to evaluate C transformation and efflux during decomposition. Complimentary laboratory incubations were performed to measure the effects of Mn enrichment on C transformation and greenhouse gas (CO_2, N_2O) production in N-fertilized and unfertilized agricultural soils. We further developed a novel biogeochemical model based on existing observations that simulates how Mn bioavailability interacts with N and warming to influence soil organic C stocks in temperate forests. We determined that Mn addition accelerated decomposition of leaf litter into CO_2 and into decomposition products that associated with minerals, and these effects were primarily observed under experimental N enrichment. Mn addition also suppressed N_2O emissions, indicating the potential for complex effects of Mn biogeochemistry on greenhouse gas emissions. Based on simulations and experiments, we predict that warming and N enrichment generate Mn limitation

to litter decomposition where Mn is poorly soluble, enabling C accumulation over decadal timescales. Through this work, we aim to establish a quantitative coupled modeling-experimental framework for evaluating geochemical controls on how C is stored, processed, and released from watersheds.

Machine Learning Model Prediction of Streamflow in Walker Branch Watershed

Dan Lu,[1,*] Natalie Griffiths,[2] and Eric M. Pierce[2]

[1]Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, TN
[2]Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN

(lud1@ornl.gov)

Project Lead Principal Investigator (PI): Eric M. Pierce

BER Program: ESS

Project: Critical Interfaces Science Focus Area (Oak Ridge National Laboratory)

Project Website: https://www.esd.ornl.gov/programs/rsfa/

Project Abstract: How will the hydro-biogeochemical function of watersheds respond to hydrologic intensification and land use/land cover change from local to regional scales? Addressing this question is crucial but also challenging. It requires large data, comprehensive model representation, and sophisticated data-model integration. Although a broad collection of diverse observations is increasing, current hydro-biogeochemical models have inadequate watershed process representation, and existing data assimilation methods are not powerful enough to incorporate diverse data for prediction.

Here we highlight the use of machine learning (ML) methods for hydro-biogeochemical simulations. ML models are powerful in extracting patterns, discovering new knowledge from multi-scale, multi-types of data, and identifying underlying cause-effect relationships for predictive understanding. We applied a ML approach, called Long Short-Term Memory (LSTM) network, to understand rainfall-runoff processes using data collected in Walker Branch Watershed (WBW). WBW is a 97.5-ha, temperate deciduous forest watershed located in East Tennessee, USA. Hydrological, biogeochemical, and ecological process studies have been carried out in this seminal research catchment since 1967. The multiple, long-term datasets that have been collected in WBW provide the opportunity to apply ML methods to predict hydrological dynamics. These long-term datasets include daily climate and soil temperature (1993-2010), precipitation (1969-2012), streamflow (1969-2014), and stream chemistry (1989-2013). We use LSTM to simulate streamflow based on meteorological and environmental observations including precipitation, air temperature, relative humidity, and soil temperature. A total of 14 years of daily data (1993-2006) were used, with the first 10 years for network training and the remaining 4 years for out-of-sample prediction. Results indicate that LSTM performed well in the training period where its predictions closely matched observed streamflow with the Nash-Sutcliffe efficiency of 0.97, although the predictions were relatively poor in 2004 and 2006. After hypothesis testing, we found that the poor performance in these two hot and dry years resulted from the lack of ET-related observations that were not included in the training and thus the relevant processes were not learned.

Here we used an interpretable LSTM which not only calculates variable importance but can also guide data collection and model development. We are working on ML model uncertainty quantification and will use the uncertainty bounds to indicate when the ML results can be trusted in the projection of future streamflow. Additionally, we are developing hybrid ML models to sufficiently leverage the data information and our domain knowledge for improving predictions.