



# Abstract Book

*for the*

## 2015 Environmental System Science (ESS) Principal Investigators (PI) Meeting

Bolger Center  
Potomac, MD  
April 28-29, 2015

Climate and Environmental Sciences Division (CESD)  
Office of Biological and Environmental Research (BER)  
Office of Science  
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# Welcome

Welcome to the 2015 Environmental System Science (ESS) Principal Investigators (PI) Meeting! This program and abstract document provides a record of the research sponsored by the Terrestrial Ecosystem Science (TES) and Subsurface Biogeochemical Research (SBR) activities which form ESS within the Climate and Environmental Sciences Division (CESD) of the Department of Energy's Office of Biological and Environmental Research (BER).

There are four broad objectives for the meeting: (1) provide opportunities to share research results and promote interactions; (2) evaluate informally the progress of each funded program or project; (3) showcase the scientific expertise and research progress to senior managers within the DOE Office of Science, the DOE technology offices, and other invited attendees from other federal agencies; and (4) start a dialogue with the scientific community on future research challenges for the BER and DOE mission areas.

The agenda for April 28-29, 2015 includes presentations from relevant BER programmatic staff, invited speakers, and members of the funded research community in plenary sessions; several concurrent/breakout sessions; and two major poster sessions. The poster session includes 11 student posters that highlight the contributions of some of the younger scientists supported by the programs. We have planned several concurrent sessions on Tuesday evening to maximize the time for technical interaction during the meeting. The meeting concludes with a plenary session designed to illustrate the interface of science and policy.

We thank you in advance for your attendance, your presentations at this year's meeting, and your continued dedication and innovation to help advance the research to address BER and DOE mission areas. We look forward to meeting with you, discussing your research results, and identifying opportunities for future challenges.

We thank Andrew Flatness of DOE/CESD and Jody Crisp, Tracey Vieser, and Marie Asher of ORAU for coordinating the logistical aspects and arrangements for the meeting.

Paul Bayer, Roland Hirsch, Mike Kuperberg, David Lesmes and Dan Stover

April 28, 2015

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**Environmental System Science  
 Principal Investigator (PI) Meeting  
 April 28-29, 2015  
 Bolger Center, Potomac, MD**



**Monday, April 27, 2015**

7:00-8:30pm **Meeting Check In (Franklin Building)**

**Tuesday, April 28, 2015**

6:30-8:00am **Breakfast (Osgood Building)**

7:00-8:00am **Meeting Check In (Franklin Building)**

8:00-9:55am **Overview of Programs and Strategic Directions (Ben Franklin Hall) Kuperberg**

8:00-8:05am Welcome and Introductory Comments.....M. Kuperberg

8:05-8:10am BER Programs.....S. Weatherwax

8:10-8:20am CESD Programs & Strategic Directions.....G. Geernaert

8:20-8:35am Science Communications.....R. Borchelt

8:35-8:50am TES Program Goals, Objectives, Activities and Highlights.....D. Stover

8:50-9:10am SBR Program Goals, Objectives, Activities and Highlights .....D. Lesmes

9:10-9:20am Accelerated Climate Model for Energy (ACME) Update.....D. Koch

9:20-9:30am Regional and Global Climate Modeling and Analyses.....R. Joseph

9:30-9:40am CESD Data Activities.....J. Hnilo

9:40-10:10am **Break**

10:10-12:15pm **Plenary Session I –Capturing the Structure and Function of Terrestrial Environments across Scales (Ben Franklin Hall) Lesmes**

10:10-10:45am From Archaea to the atmosphere: Can genome-scale resolution improve earth system models of climate change?..... S. Saleska

10:45-11:15am Subsurface sensing is hotting up! Heated fiber optics for water content and flux in the subsurface from 0.1 to 10,000m.....J. Selker

11:15-11:45am Nutrient cycle impacts on forest ecosystem carbon cycling.....J. Fisher

11:45-12:15pm Google Earth Engine.....D. Thau

12:15-2:00pm **Lunch (Osgood Building)**

12:30-2:00pm Lunch with Facilities & Community Resources

EMSL/JGI (Room 18/19).....N. Hess/S. Tringe

ARM/AmeriFlux (Room 17A/17B)..... L. Berg and M. Torn

Google Earth Engine discussion and demonstration (Room 17 A/B).....D. Thau

2:00-5:00pm **Poster Session I (Franklin Building: Rooms 9A/B, 15/16, 20 and 21)**

2:00-3:30pm Poster Subsession A

3:30-5:00pm Poster Subsession B

5:30-7:00pm **Dinner (Osgood Building)**

7:00-8:30pm **Concurrent Sessions - I (Franklin Building)**

*Concurrent Session 1: Recent Advances in Tropical Ecosystem Research (Room 18/19)* **Stover**

7:00-7:20pm NGEE Tropics Update.....J. Chambers

7:20-7:40pm Tropical Response to Altered Climate Experiment (TRACE): Adventures in warming a wet tropical forest in Puerto Rico.....T. Wood

7:40-8:00pm Ecophysiological controls on Amazonian precipitation seasonality and variability.....J-E. Lee

8:00-8:20pm Drivers of redox biogeochemistry in humid tropical forests.....W. Silver

8:20pm Discussion

8:30pm Adjourn

*Concurrent Session 2: Environmental Microbiology (Room 1)* **Bayer**

7:00-7:20pm Toward a predictive understanding of the response of belowground microbial carbon turnover to climate change drivers in a boreal peatland.....J. Kostka

- 7:20-7:40pm Microbial diversity and greenhouse gas dynamics in coastal wetlands.....S. Tringe
- 7:40-8:00pm The diversity and possible subsurface biogeochemical roles of enigmatic bacteria and archaea from massive candidate phyla radiations.....J. Banfield
- 8:00-8:20pm Efforts towards understanding the links between microbial community structure and function within ENIGMA.....D. Elias
- 8:20pm Discussion
- 8:30pm Adjourn

*Concurrent Session 3: Land-Atmosphere Interactions* (Room 17 A/B) **Lesmes/McFarlane**

- 7:00-8:30pm Moderated discussion by Larry Berg and Margaret Torn on approaches for improving the understanding of land-atmosphere interactions at ARM and Ameriflux sites.
- 8:30pm Adjourn

*Concurrent Session 4: Next Generation Sensors, Networking, Data Assimilation and Modeling*  
(Ben Franklin Hall) **Hirsch**

- 7:00-7:05 Session Introduction.....M. Mayes
- 7:05-7:15pm Translating sensing technological opportunity into environmental understand from the Dead Sea to Africa (Oregon Statue Univ).....J. Selker
- 7:15-7:25pm The NGEE Arctic Tram for fine resolution observations of surface energy and vegetation properties (NGEE Arctic).....S. Wullschleger/M. Torn
- 7:25-7:35pm Role of continuous field measurements in determining deep soil carbon response to warming (LBNL TES SFA).....P. Nico
- 7:35-7:45pm NMR sensors for *in-situ* monitoring of soil moisture content (Vista Clara, Inc.).....D. Walsh
- 7:45-7:55pm SPRUCE: Automated measurement systems and their management in support of large-scale manipulations (SPRUCE).....P. Hanson
- 7:55-8:05pm HD TomoGPR: Ground Penetrating Rada system for fine root analysis (RNET Technologies).....G. Sabin
- 8:05-8:15pm Above and below ground hydrogeophysical monitoring and simulation to quantify coupled hydrological and thermal processes important for carbon cycling (LBNL SBR SFA).....B. Dafflon

- 8:15-8:25pm High frequency measurements to inform solute source areas within a Catchment (ORNL SBR SFA).....S. Brooks
- 8:25-8:35pm Autonomous, high-performance computing enabled 4E electrical resistivity monitoring (PNNL SBR SFA).....T. Johnson
- 8:35-8:45pm Sensor network for modular ecosystem model development (ORNL TES SFA).....D. Wang
- 8:45-9:00pm Open Forum and Discussion.....All
- 9:00pm Adjourn

**Wednesday, April 29, 2015**

- 6:30-8:00am **Breakfast (Osgood Building)**
- 8:00-9:00am **Plenary Session II: Advancements from DOE Early Career Awards (Ben Franklin Hall)** **Lesmes**
- 8:00-8:15am Geospatial representation of the circumarctic-scale permafrost carbon feedback.....D. Hayes
- 8:15-8:30am Computational Bayesian framework for quantification of predictive uncertainty in environmental modeling.....M. Ye
- 8:30-8:45am Quantifying river dynamics and floodplain exchanges using remotely sensed imagery.....J. Rowland
- 8:45-9:00am Multi-system analysis of microbial biofilms.....M. Marshall
- 9:00-12:00pm **Poster Session II (Franklin Building: Rooms 9A/B, 15/16, 20 and 21)**
- 9:00-10:30am Poster Subsession C
- 10:30-12:00pm Poster Subsession D
- 12:00-1:30pm **Lunch (Osgood Building)**
- Radionuclides Working Group (Room 1).....B. Powell
- 1:30-2:30pm **Plenary Session III – Advances in Radionuclides Research (Ben Franklin Hall)** **Hirsch**
- 1:30-1:50pm Fe and S biogeochemistry in redox dynamic environments; progressing towards a predictive understanding of U biogeochemical transformations.....K. Kemner

1:50-2:10pm Subsurface biogeochemistry of actinides.....A. Kersting

2:10-2:35pm Molecular coupling between subsurface organic matter, sediment microbial processes, and uranium biogeochemistry.....J. Bargar

2:30-4:00pm **Concurrent Sessions – II (Franklin Building)**

*Concurrent Session 5: Advances in Soil Organic Matter Research (Room 1)* **Stover**

2:30-2:50pm Innovative FT-ICR MS approaches to the analysis and interpretation of soil organic matter.....M. Tfaily

2:50-3:10pm News from a whole-profile soil warming experiment.....M. Torn

3:10-3:30pm Multifunctional roles of natural organic matter in biogeochemical transformation of metals.....B. Gu

3:30-3:50pm Belowground C allocation and plant-microbe interactions in two contrasting boreal peatlands.....A. Finzi

3:50pm Discussion

4:00pm Adjourn

*Concurrent Session 6: Dynamic Vegetation & Trait-Based Modeling (Room 17 A/B)* **Kuperberg**

2:30-2:50pm Dynamic Global Vegetation Model activities???.N. McDowell

2:50-3:10pm NGEE-Tropics trait-based modeling.....C. Koven

3:10-3:30pm Root trait modeling.....C. Iverson

3:30-3:50pm Functional trait work in???.P. Reich

3:50pm Discussion

4:00pm Adjourn

*Concurrent Session 7: Multi-scale Watersheds (Ben Franklin Hall)* **Lesmes**

2:30-2:35pm Introduction.....D. Lesmes

2:35-2:39pm Genomes-to-Watershed LBNL SFA 2.0 snapshot.....S. Hubbard

2:39-2:51pm A floodplain perspective on subsurface nitrogen cycling.....K. Williams

- 2:51-3:03pm Genome-scale characterization of subsurface microbial activity relevant to the nitrogen cycle.....H. Beller
- 3:03-3:15pm Multi-scale, genome-informed approach to modeling the subsurface carbon-nitrogen cycle.....C. Steefel
- 3:15-3:19pm PNNL Subsurface Biogeochemistry SFA snapshot.....J. Zachara
- 3:19-3:37pm Temporal and spatial dynamics of groundwater and surface water exchange..T. Johnson
- 3:37-3:55pm Multi-scale biogeochemical processes and modeling.....C. Liu
- 4:00pm Adjourn

*Breakout Session 8: Methane/Hydrobiogeochemistry (Room 18/19)*

**Bayer**

- 2:30-2:50pm Seasonal oxygen dynamics in a thermokarst bog in interior Alaska: Implications for rates of methane oxidation.....R. Neumann
- 2:50-3:10pm Initial responses of methane cycling to deep peat warming in a Minnesota bog.....J. Keller
- 3:10-3:30pm Spatial constraints in microbial processes controlling carbon mineralization in soils.....S. Fendorf
- 3:30-3:50pm Methane emissions from upland forests.....S. Pitz
- 3:50pm Discussion
- 4:00pm Adjourn

**4:15-5:30pm Plenary Session IV – Arctic Science and Policy (Ben Franklin Hall)**

**Kuperberg**

- 4:15-4:30pm NGEE-Arctic - capturing process understanding in large-scale models  
.....Stan Wullschleger (Oak Ridge National Laboratory)
- 4:30-4:45pm Arctic Council - translating science to inform adaptation actions in the Arctic  
.....Tom Armstrong (Madison River Group)
- 4:45-5:00pm Arctic research and international relations .....Adrianna Muir (Department of State)
- 5:00-5:15pm Arctic research and US perspectives.....Simon Stevenson  
(White House, Office of Science and Technology Policy)

5:15-5:30pm           **Closeout/Announcements**

5:30-7:00pm           **Dinner (Osgood Building)**

7:00pm                 **Adjourn**

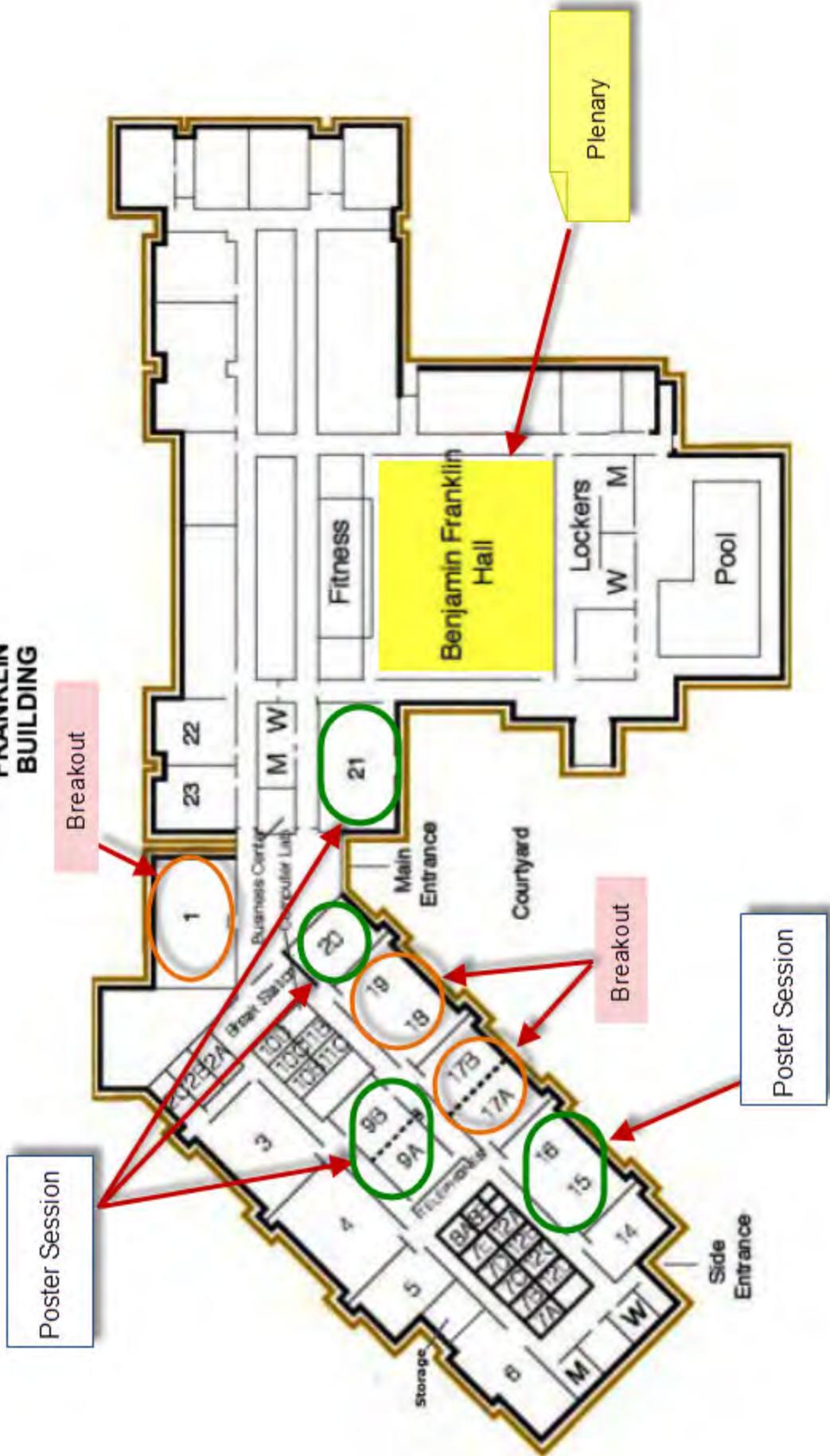
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7:00pm NGEE-Arctic (Room 17 A/B).....S. Wullschleger

7:00pm SPRUCE (Room 18/19).....P. Hanson

**FRANKLIN BUILDING**



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# Student Abstracts

## **Integrated Surface-Subsurface Reactive Transport**

In natural surface-subsurface systems, areas of disproportionately high reaction rates often heavily influence total elemental fluxes. These pockets of high reaction rates tend to occur at interfaces, such as the capillary fringe or hyporheic zone, where a hydrologic flowpath converges with either a chemically distinct hydrologic flowpath or a reactive substrate. Understanding the affects that these highly reactive zones have on the behavior of shallow subsurface systems is integral to the accurate quantification of nutrient fluxes and biogeochemical cycling. The numerical simulation of many of these areas of disproportionately high reaction rates requires an integrated surface-subsurface modeling approach. Here we present recent developments to the massively parallel reactive transport code ParCrunchFlow. This model, previously applicable only to steady-state, saturated subsurface flows, has been extended to transient, surface-subsurface environments, allowing the numerical simulation of reactive transport processes in highly-heterogeneous, field-scale systems. Proof-of-concept simulations involving the biogeochemical cycling of carbon (C) and nitrogen (N) in both hillslope and floodplain settings are presented.

### **Peer Reviewed Publications**

**Beisman, J.**, Maxwell, R., Navarre-Sitchler, A., Steefel, C., Molins, S. ParCrunchFlow: An Efficient, Parallel Reactive Transport Simulation Tool for Physically and Chemically Heterogeneous Saturated Subsurface Environments. *Computational Geosciences*, In Review.

### **Awards**

2013 Edna Bailey Sussman Grant Recipient

### **Conference Presentations**

**Beisman, J.**, Maxwell, R., Navarre-Sitchler, A., Steefel, C., Molins, S. High-resolution reactive transport: A coupled parallel hydrogeochemical model. GSA Annual Meeting, Paper No. 245-27, Denver, CO, October 2013.

**Beisman, J.**, Maxwell, R., Navarre-Sitchler, A., Steefel, C., Molins, S. High-resolution reactive transport: A coupled parallel hydrogeochemical model. AGU Fall Meeting, Abstract H43D-1468, San Francisco, CA, December 2013.

**Beisman, J.**, Maxwell, R., Navarre-Sitchler, A., Steefel, C., Molins, S. High-resolution reactive transport: A coupled parallel hydrogeochemical model. Goldschmidt 2014, Abstract 3232, Sacramento, CA, June 2014.

**Beisman, J.**, Maxwell, R., Navarre-Sitchler, A., Steefel, C., Molins, S. High-resolution reactive transport: A coupled parallel hydrogeochemical model. CMWR 2014, Submission ID 3232, Stuttgart, Germany, June 2014.

**Beisman, J.**, Maxwell, R., Navarre-Sitchler, A., Steefel, C. Implementation of positivity-preserving, high order advection schemes in a reactive transport model. AGU Fall Meeting, Abstract H41F-0898., San Francisco, CA, December 2014.

### **Workshops**

Participant, Expanding the Role of Reactive Transport Modeling within the Biogeochemical Sciences Workshop, Alexandria, VA, April, 2014.

## **“The Microbes Underground: A Look at Subsurface Nitrogen-Cycling Microbial Communities at Uranium Contaminated Sites in the Colorado River Basin”**

**Emily Cardarelli, John Barger, and Christopher Francis**

### **Abstract**

Throughout the upper Colorado River Basin (CRB), uranium persists as a relic contaminant of former ore processing activities. Elevated solid-phase uranium levels exist in fine-grained, organic-rich sediments intermittently found within the floodplain alluvium of the following Department of Energy-Legacy Management sites: Rifle, CO; Naturita, CO; and Grand Junction, CO. Coupled with seasonal groundwater fluctuations that alter the subsurface redox conditions, previous evidence from Rifle, CO suggests this resupply of uranium may be controlled by biologically-produced nitrite and nitrate. Known as nitrification, the two-step process of archaeal and bacterial ammonia-oxidation is followed by bacterial nitrite oxidation, generating nitrate under oxic conditions. Our hypothesis is that when seasonally elevated groundwater levels recede and the subsurface system becomes anoxic, the nitrate diffuses into the reduced interiors of organic-rich sediments and becomes readily available for denitrification, the stepwise anaerobic reduction of nitrate/nitrite to dinitrogen gas. Denitrification may then be coupled to the oxidation of sediment-bound U(IV) forming mobile U(VI), allowing it to resupply uranium into local groundwater supplies. One key step in substantiating this hypothesis is to demonstrate nitrogen-cycling organisms are present in the organic-rich sediments.

Here we investigate how the diversity and abundances of nitrifying and denitrifying microbial populations change throughout the organic-rich, fine-grained sediments of the subsurface by using functional gene markers for ammonia-oxidation (*amoA*, encoding the  $\alpha$ -subunit of ammonia monooxygenase) and denitrification (*nirK*, *nirS*, encoding nitrite reductase). Abundances of these key nitrogen cycling functional genes are specifically targeted and determined through quantitative polymerase chain reaction (qPCR), elucidating how relative numbers of nitrifiers (*amoA*) and denitrifiers (*nirK*, *nirS*) vary with depth, vary with location, and relate to uranium release in sediment cores spanning the upper CRB. Early findings at Rifle, CO indicate subsurface archaeal *amoA* diversity spans Group 1.1b, and includes soil, freshwater, and estuarine relatives. These results suggest a robust community of ammonia-oxidizing archaea are present and their products may participate in uranium mobilization.

## The Effect of Natural Organic Matter on Plutonium Sorption to Goethite

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The effect of natural organic matter (NOM; citric acid, Deferoxamine B (DFOB), Suwannee River fulvic acid, and Leonardite humic acid) on plutonium sorption to goethite was studied using batch sorption experiments at  $5 \text{ mg}_C \cdot \text{L}^{-1}$  and  $50 \text{ mg}_C \cdot \text{L}^{-1}$  NOM,  $10^{-10} \text{ M}$  plutonium, and  $0.1 \text{ g} \cdot \text{L}^{-1}$  goethite concentrations. Aqueous concentrations of both plutonium and NOM in the bulk solution were monitored by liquid scintillation counting (LSC) in order to understand the extent of NOM and plutonium sorption to goethite and possible ternary complex formation. This was made possible through the utilization of radiolabeled NOM where possible. Commercially available  $^{14}\text{C}$ -citric acid was purchased, while fulvic acid and humic acid were labeled with tritium as a part of this study using tritiated  $\text{NaBH}_4$  to reduce NOM ketones to secondary alcohols while minimally affecting structure or reactivity. DFOB could not be labeled by the same mechanism, as it lacks ketones, and no radiolabeled DFOB is commercially available. Therefore DFOB sorption was determined by total organic carbon analysis in a separate plutonium free experiment.

These data indicate that NOM type, NOM concentration, and system pH have significant impacts on plutonium sorption, as well as the underlying sorption mechanisms. All the NOM studied reduced plutonium sorption from near pH 4 to the point of zero charge of goethite ( $\sim \text{pH } 8$ ). Citric, fulvic, and humic acids decreased aqueous plutonium concentrations below pH 4 presumably through ternary complex formation with the goethite surface or, in the case of humic acid, by incorporation into coagulating NOM complexes. In systems above pH 8, competition between Pu(IV) hydrolysis and complexation by NOM was apparent and resulted in an increase in sorption and a decreased solubilizing effect of the NOM.

Mechanisms for ternary complex formation were characterized by Fourier transform infrared (FTIR) spectroscopy in the absence of plutonium. For this study, high concentrations of NOM ( $2.5 \text{ g}_C \cdot \text{L}^{-1}$ ) were mixed for several days with goethite and the pH regularly adjusted to  $\sim 4.5$ . The solid fraction of these suspensions were lyophilized and the powder was analyzed by attenuated total reflectance FTIR spectroscopy. Citric and fulvic acids demonstrated clear surface interactions with goethite near pH 4.5 whereas no DFOB interactions were observed. The observation of no/limited DFOB interactions with goethite is consistent with batch sorption data at all the pHs studied. Spectra indicate significant homoaggregation of humic acid and little goethite surface interaction near pH 4.5. These data augment that of the batch sorption experiments in determining the mechanisms of plutonium removal from the bulk aqueous solutions either by 1) binary sorption to the goethite surface 2) NOM assisted sorption to the goethite surface 3) incorporation into an NOM aggregate. These data also indicate that plutonium sorption to goethite can be either enhanced by formation of ternary surface complexes at low pH or reduced via formation of soluble plutonium-NOM complexes. The former has implications for colloid facilitated transport of plutonium where the NOM may stabilize iron mineral colloids and also provide strong association of plutonium with the colloids.

Extended x-ray absorption fine structure (EXAFS) spectroscopy was used to study the coordinating environment of plutonium sorbed to goethite under conditions suggested by batch sorption and FTIR spectroscopic data to result in ternary complex formation. EXAFS data support the formation of a ternary, goethite-plutonium-citrate, complex near pH 4.

## **Quantifying nonstructural carbon pools in temperate forest trees**

### **Project Summary:**

Like all woody plants, trees store nonstructural carbon (NSC), primarily consisting of sugars and starch, as reserves to support growth and metabolism. The importance of this storage lies in the fact that immobile, long-lived trees can draw on these reserves in order to cope with times of stress, including exposure to drought, pests and disease, disturbance, and climate extremes. Thus, NSC is remarkably relevant when predicting forest responses and resiliency to global climate change, and has an influence at multiple scales from individual tree survival to carbon cycling in whole forest ecosystems. However, important questions about the size, turnover, and availability of NSC remain unanswered. These knowledge gaps lead to large uncertainty about how to represent carbon allocation and storage processes, and have implications for model forecasts of terrestrial ecosystem feedbacks to atmospheric CO<sub>2</sub> under future climate scenarios.

The primary objective of this work is to construct detailed budgets of the size, turnover, and availability of the mobile C pool in temperate forest trees in New England. Field sampling at Harvard Forest along with laboratory analyses will allow for the quantification of NSC at the individual tissue level, which will then be scaled up to determine whole-tree and whole-ecosystem NSC budgets. In 2015, we will be collecting samples for radiocarbon analysis to estimate turnover time (i.e. mean age) of NSC stored in different tissues, and to better understand mixing between new (recent photosynthate) and old NSC. These data will be used to test a multi-pool model representation of storage in forest trees. Using this data to improve models of tree carbon dynamics will enhance our understanding of the capacity for trees to tolerate abiotic and biotic stressors as well as our ability to predict forest responses to global climate change.

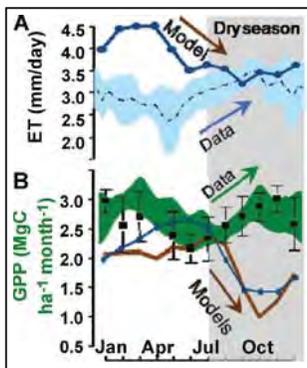
### **Personal Contribution:**

I am currently a second year Ph.D. student in Andrew Richardson's laboratory at Harvard University. This project comprises a major portion of my thesis work, which more generally focuses on the storage of nonstructural carbon reserves in woody plants. After joining the laboratory in the fall of 2013, I began leading this work at Harvard Forest. As project lead, I direct field sample collection, sample processing, and data analysis.

Throughout 2014, I collected root cores, stem cores, and branch samples monthly from 24 trees of 5 dominant New England species at Harvard Forest (Petersham, MA), yielding nearly 2,000 samples. My role was to organize, prepare for, and lead each sample collection. Generating this dataset which includes multiple tree species, high temporal resolution, and a broad range of tissue types is essential to support the improvement and development of models that represent carbon allocation and storage processes.

With the completion of sample collection in December 2014, I have shifted my focus to processing these samples. I am supervising a female Harvard University undergraduate student, and we will conduct all of the laboratory analyses for this project. I have already obtained NSC concentrations from 2014 branch samples, and this data will be presented on my poster at ESS. I will use tissue level concentrations of NSC and allometric equations to scale-up to whole-tree budgets and then extrapolate to whole-ecosystem budgets using forest inventories. These data will be used to test existing ecosystem model predictions (e.g. PnET, FÖBAAR) of seasonal dynamics of NSC, as well as hypotheses related to differences between evergreen and deciduous, and ring porous and diffuse porous hardwood species. I will take the lead on publishing these results and sharing them at the annual conference of the American Geophysical Union.

**Background:** The frequency and intensity of extreme weather events (e.g. droughts/floods/heat waves) are predicted to increase in the coming decades as a consequence of increased carbon dioxide, causing major consequences for cities, people and natural ecosystems [3]. General Circulation Models (GCMs) and Land Surface Models (LSMs) are used to forecast climate variability and land surface coupled response, however, many of the models' key components, which relate to land and atmospheric interactions, (e.g. processes contributing to the carbon cycle and controls on the hydrologic cycle) are still not well characterized [4][5][7]. For instance, in Central Amazonia the models fail to represent the correct seasonal cycle of evapotranspiration (ET) and Gross Primary Production (GPP) and typically display peaks in the wet season contrary to observations made in the field (Fig.1a)[2]. Similarly the seasonal cycle of phenology in wet tropical forests tends to be exaggerated by models and in reality is much less apparent (Fig.1b)[2][6]. It is crucial to understand if tropical forests will remain CO<sub>2</sub> sinks in the future, and the model biases have major



**Figure 1** Differences between IBIS LSM (brown), NCAR GCM and Community Land Model (blue) and eddy covariance observations made in the Tapajos National Forest of ET (A) and GPP (B) [2]

implications for our ability to make forecasts in these regions. Based on these deficiencies, the following aims were identified for this study.

**Aim 1 Analysis of Remote Sensing Datasets:** Through remote sensing products we were able to estimate net radiation, precipitation, photosynthesis, phenology, cloud coverage, temperature, ET, soil moisture, vegetation water content (from microwave imagery), and groundwater. These are in turn used to understand the interrelationships between these components such as the energy vs. water control of photosynthesis.

**Aim 2 Comparing findings from Aim 1 with GCM data:** I will compare my remote sensing analysis with outputs from GCMs (CMIP5) and uncoupled LSMs to determine regions of strong biases and their causes (e.g. overestimation of water and radiation stresses). This will be critical in tropical forests due to their major role as CO<sub>2</sub> sinks. In the wet tropics, the seasonality of GPP and ET is typically shifted (Fig. 1), leading to an inaccurate forecast of net primary productivity (NPP) and water flux sources and sinks.

**Contribution to GOAmazon:** In my research I am using remote sensing analysis to better understand plant physiological response and processes and how they affect the carbon and hydrologic cycles. Additionally, in summer 2015 I will be part of a field campaign to several of the GOAmazon field sites with collaborators Joseph Berry (Carnegie Institution), Jung-Eun Lee (Brown), Ben Lintner (Rutgers), Laura Borma (INPE), Rafael Oliveira (University of Campinas) and Tomas Domingues (University of Sao Paulo) to perform *in situ* measurements (vegetation water stress, flux measurements and radiosondes) to gather information on plant physiological water stress, fluorescence and to validate the remote sensing data.

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## **Mapping AmeriFlux footprints: Towards footprint model processing across a network of flux tower sites**

In this research project, I addressed the feasibility and challenges of footprint model application across a wide range of biomes within the AmeriFlux network. Footprint models provide source calculations to attribute ecosystem fluxes to specific surface areas. Such calculations are needed for data synthesis studies and can support flux up-scaling to larger regions, for example, when combined with remote sensing data. However, flux footprints are not currently being routinely processed; different approaches exist but have not been standardized yet. In part, this is due to varying instrumentation and data processing methods at the site-level, resulting in heterogeneous data sets. The goal of this work was to evaluate tower footprint models across different sites, aiming at a future AmeriFlux product to be generated at the network level.

My key contributions to this project included data assimilation and processing, footprint model evaluation using statistical and visualization techniques, as well as the implementation of parallelized processing routines. First, the data processing involved inquiring for specific footprint model input variables not currently in the database and directly contacting principal investigators. This was crucial to understand site specific parameters, and also to formulate which meta data will be needed for the implementation of standardized processing routines. I summarized which variables commonly collected at flux tower sites will be needed as model input. In turn, this led to the decision to include variables such as the variance of the cross wind speed in future releases of the data base. In addition, reaching out to the scientific community resulted in several new sites joining the AmeriFlux network.

Next, I evaluated the following two different models to compute flux footprints. The model by Kormann & Meixner (2001) calculates an analytical solution of the advection-diffusion equation in the surface layer. It uses an exponential mean wind profile, an eddy diffusivity and Monin Obukhov similarity theory. By comparison, the model by Kljun et al. (2004) is a parameterisation of model calculations from a three-dimensional Lagrangian particle dispersion over a range of atmospheric stratifications from advective to stable. Both models can estimate crosswind integrated (one-dimensional) and crosswind distributed (two-dimensional) representations of the theoretical footprint functions.

After the footprint model code was integrated into a processing framework, I implemented a parallelization of the footprint calculations which was important to speed up the evaluation of several tower sites in synthesis. Preliminary results for six AmeriFlux and two ICOS sites show reasonable agreement among the different footprint models for daytime unstable atmospheric conditions, and larger differences during nighttime stable conditions. Overall, there was higher variability in footprint estimates at night compared to daytime, predominantly during winter. Along with providing a summary report to the participating investigators, I produced animated maps in video format that show the progression of the crosswind distributed footprints for several years of data and can be used for data interpretation within the AmeriFlux database. One of the principal investigators directly forwarded these maps to the forest service, showing where flux source areas are predominantly located at his site, in the hope for the re-assessment of a planned logging of trees.

I presented preliminary results of this study at the American Geophysical Union (AGU) Fall Meeting in December 2014 and at the North American Carbon Program (NACP) Principal Investigator Meeting in January 2015. At the NACP meeting, I also presented the work as an example case study during a breakout session on interoperability and synergy effects between research networks.

# Microbiological-enhanced mixing by long-range extracellular electron transfer during in-situ bioreduction of uranium

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## ABSTRACT

Bioreduction is a promising strategy for the long-term management of groundwater contaminated by metals and radionuclides, for which conventional treatments may be ineffective, ecologically damaging, or prohibitively expensive to implement at larger scales. For example, it is a suitable remediation technique for the immobilization of hexavalent uranium, which is difficult to treat by conventional means due to the large area of contamination that currently exceeds 2 million acres. By amending the affected areas with an electron donor such as acetate or ethanol, native bacteria capable of dissimilatory metal reduction are able to grow by coupling the oxidation of donor with the reduction of uranium. The reduced product is insoluble, immobile, and less toxic than the reactant.

Physical models have accounted for various aspects of hydrology, geochemistry, and microbiology to predict the extent of bioreduction, but all to date have excluded the potential contribution of long-range extracellular electron transfer (EET) by bacteria that may exceed the zone of physical mixing between electron donor and acceptor. Long-range EET by metal-reducing bacteria is a recently discovered phenomenon that occurs via electron shuttling, or along the length of conductive pili called 'nanowires'. Nanowires are known to extend tens of micrometers from the cell and form conductive biofilms, but their contribution to metal reduction has not been adequately tested under field conditions using chemicals and concentrations representative of the groundwater environment.

Using a novel microfluidic reactor that I designed and fabricated in my lab, and manganese dioxide as a surrogate for uranium, I am investigating the role of long-range EET in bioremediation. In particular, I hope to determine 1) the distance of nanowire penetration of nanopores 2) the concentration threshold below which nanowires and electron shuttles are produced, and 3) the relative contribution of each under different flow regimes. Preliminary results from the first task indicate that reduction of metals and radionuclides may be underestimated due to the neglect of long-range EET in field models. I am actively working on the remaining tasks to gain insight into the chemical triggers that promote EET and the role that groundwater flow has in selecting between different EET mechanisms. Greater understanding of long-range EET phenomena as a result of my experiments has the potential to improve the predictive power of field models, reduce the cost of bioreduction, and lead to engineered strategies that are more efficient than the current standard.

## Roots and mycorrhizal fungi differentially impact microbial processes

Jessica A. M. Moore

**Project Summary.** Plant roots, their associated mycorrhizal community, and the free-living microbial community interact to regulate the movement of carbon from soil to the atmosphere, one of the most important and least understood fluxes of terrestrial carbon. Our understanding of how plant-microbial interactions alter soil carbon decomposition is lacking, leading to poor model predictions of terrestrial carbon feedbacks to the atmosphere. I tested how roots, mycorrhizal fungi, and the free-living microbial community alter soil carbon decomposition and predicted roots and mycorrhizal fungi would additively increase microbial activity. I manipulated the access of roots and mycorrhizal fungi to bulk soils *in situ* in a temperate mixed deciduous forest. I added  $^{13}\text{C}$ -labelled substrate to trace carbon through respiration and measured microbial extracellular enzyme activity.

Cellobiohydrolase activity was equally high when the free-living microbial community was degrading soil carbon alone as when microbes were in the presence of both roots and mycorrhizal fungi. Cellobiohydrolase activity was lowest when mycorrhizal fungi were present with the free-living community, but roots were excluded. I found that microbial biomass was negatively correlated with peroxidase activity and mycorrhizal biomass was positively correlated with phenol oxidase activities. My results indicate soil carbon decomposition rates were contingent upon root-mycorrhizal-microbial interactions and, when excluded from roots, mycorrhizal fungi reduced microbial decomposition of soil carbon. Some of the heterogeneity in soil decomposition rates observed in nature may be explained by shifting interactions among roots, mycorrhizal fungi, and the free-living soil community. Understanding heterogeneity of plant-mycorrhizal-microbial interactions can improve predictive abilities of decomposition models.

**Student Contribution.** This DOE-funded project is central to my dissertation research program, which asks how plant-microbe interactions influence soil carbon dynamics. I helped conceive the project objectives and experimental design. I designed, constructed, and installed root and mycorrhizal exclusion PVC mesocosms at four field sites over two years. I added  $^{13}\text{C}$  substrates to soil and collected necessary gas and soil samples. I trained three undergraduate students, a post-doc, and our lab technician to aid me in procedures such as chloroform fumigation for measurement of microbial biomass, soil enzyme assays, and isolation of soil carbon fractions. I managed data collected at each of four field sites and analyzed it after discussing appropriate analyses with the project team. I presented results from this project at the Ecological Society of America 2014 meeting and submitted a first-authored manuscript on these data to *Journal of Ecology*.

## Soil microbial community shifts in response to soil thermal insulation in moist acidic tundra of Northern Alaska

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DOE-TES project

ER65188-1038283-0018377

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In the Arctic tundra, shifts in plant species composition and distribution have been observed in response to increased precipitation, soil warming, and the subsequent increases in active layer depth. Initial abiotic changes provide soil microorganisms access to previously unavailable soil organic matter via thawing soils, increasing soil microbial decomposition and nutrient mineralization rates and resulting in soil organic carbon loss and increased nutrient availability. Here we examine how microbial communities respond to increases in soil thermal insulation due to accumulation of winter precipitation at a snowfence installed in 1994 at Toolik Field Station, Alaska. We hypothesize that soil microorganisms are eliciting vegetation response through the release of nutrients under warmer conditions, providing a competitive advantage to N-rich woody species over herbaceous species. Changes in plant litter and increasing NPP may contribute to SOC re-accumulation and alter microbial community composition. Bacterial phylogeny and relative abundances from soils collected in August of 2012 were determined by 16S rRNA amplicon sequencing of extracted DNA. We found significant shifts in relative abundances of bacteria between snow depth treatments (DEEP, INT, LOW) and the control in both soil horizons (organic and mineral). The most notable shifts include in a decrease in *Verrucomicrobia* of the family Chthionobacteraceae in the mineral horizon of the DEEP zone, an increase in Chloroflexi of the family Anaerolinaceae in both organic and mineral horizons of the DEEP zone, and a highly significant decrease in Actinobacteria in the organic horizon. To investigate potential functional changes within the microbial community, we utilized the software package PICRUSt, able to infer the genetic potential of the community using ancestral state reconstruction based on the phylogenetic data obtained from 16S rRNA sequencing. This analysis revealed a trend of less abundant enzymatic genes responsible for SOM decomposition in all treatment zones relative to the control in the organic horizon, and more abundant genes in the INT and LOW zones relative to the control in the mineral horizon. This suggests soil microbial communities in surface layers are not genetically equipped to degrade organic matter from newly dominant plant species, while communities in deeper soil layers rely on older organic matter released from permafrost thaw, supporting our hypothesis of nutrient release facilitating observed vegetation shifts. These changes in microbial community composition and functionality in response to simulated future climate conditions may substantially alter carbon and nutrient cycling in the ecosystem, initiating a cascade of biotic and abiotic effects.

## Increased Nitrogen availability in a tundra ecosystem during five years of permafrost thaw

Student Presenter: Verity G. Salmon, University of Florida Biology Department, Gainesville, FL

Primary Investigator: Dr. Edward A.G Schuur, Northern Arizona University, Flagstaff, AZ

The globally significant size of the permafrost carbon (C) pool reflects the balance between soil decomposition and plant growth in high latitude ecosystems. Projected increases in mean annual temperatures in these cold ecosystems are expected to increase rates of both C uptake and release. The Carbon in Permafrost Experimental Heating Research (CiPEHR) is a manipulative warming experiment started in the winter of 2008 to enhance our understanding of tundra ecosystems experiencing permafrost thaw. Soil warming at CiPEHR is applied in the winter using snow fences that increase insulation against cold winter air temperatures. Higher soil temperatures translate to deeper thaw during growing season; as a result the active layer thickness in soil warmed plots has progressively increased every year of the experiment (2.8 cm deeper than control in 2009, 11.5 cm deeper than control in 2013). An air warming treatment is applied during the growing season using open top chambers that warm the air above plots an average of 0.4°C. My dissertation research focuses on changes in N cycling between plants and soils during the process of permafrost thaw. Nitrogen (N) is expected to play a key role in determining the future balance of soil C losses and increased C sequestration by plants because it is the main nutrient limiting plant productivity and soil organic matter decomposition in high latitude ecosystems. Within the context of the CiPEHR experiment, my research has been comprised of plant surveys, foliar sample collection, continuous environmental monitoring and analysis of ion binding resin bags that measure the availability of inorganic N forms in surface soils. I have also performed off-plot harvests that improve upon existing site and species specific allometric relationships that allow aboveground biomass to be calculated with greater accuracy. Results from this research show a significant increase in aboveground plant biomass with five years of soil warming ( $p < 0.05$ ) that is primarily driven by the growth of the dominant tussock forming sedge, *Eriophorum vaginatum*. Analysis of *Eriophorum* foliar samples collected at peak growing season show no significant change in the %N during any of the five years of warming. Resin bags deployed at 10cm depth in the soil profile for the 2012 and 2013 growing seasons demonstrate a significant increase in available inorganic N associated with soil warming ( $p < 0.05$ ) as well a significant increase with air warming ( $p < 0.05$ ). Interestingly, resin data also show a significant negative interaction between the two treatments ( $p < 0.01$ ). Together, these results suggest that 1) Plant access to N has increased with permafrost thaw in the soil warming treatments and 2) Combined air and soil warming treatments limit N cycling and potentially productivity. Isotopic analysis of *Eriophorum* foliar samples showed no effect of warming treatments on the foliar  $\delta^{13}\text{C}$  signature, signifying water stress does not explain the diminished response in combined treatment plots. The foliar  $\delta^{15}\text{N}$  signature of *Eriophorum*, however, does decrease with soil warming throughout the course of the five year experiment ( $p < 0.05$ ). This indicates that the soil source or microbial pathway through which *Eriophorum* is acquiring N is changing as the thaw depth progresses downwards. Such a dramatic change in the N cycle bodes well for plant productivity under warmer conditions but this shift has the potential to remove the current N limitation of the microbial community in surface soils, further reducing the C storage capacity of these thawing soil profiles.

## Interactions between nitrogen fixation and methane cycling in boreal peat bogs

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Microbial N<sub>2</sub> fixation supplies an important nitrogen input to boreal peatlands, extremely oligotrophic ecosystems dominated by *Sphagnum* mosses. In this study, we coupled major and trace nutrient analyses, potential rate measurements, gene amplicon and omics sequencing to characterize interactions between N<sub>2</sub> fixation and CH<sub>4</sub> cycling at the S1 peat bog in Marcell Experimental Forest (Minnesota, USA). Total dissolved nitrogen (NO<sub>3</sub><sup>-</sup>+NO<sub>2</sub><sup>-</sup>+NH<sub>4</sub><sup>+</sup>) and phosphate were both consistently < 2 μM in surface peat, suggesting severe nutrient limitation. While dissolved Fe was 18-35 μM, Mo, V and Cu were extremely scarce (2-40 nM), suggesting that alternative metalloenzymes containing Fe in place of other metals may be expressed. However, few alternative nitrogenase transcripts were recovered with both primer and omics approaches, suggesting that Mo is likely still required for the nitrogenase cofactor despite its scarcity in peat bogs. Diazotrophy measured by both <sup>15</sup>N<sub>2</sub> incorporation and the acetylene reduction assay was 7-fold higher in anoxic than oxic incubations. No significant difference in N<sub>2</sub> fixation rates measured by either method was observed with or without 1% CH<sub>4</sub>. Anoxic <sup>15</sup>N<sub>2</sub> incorporation was 3-4x higher in treatments lacking C<sub>2</sub>H<sub>2</sub>, suggesting that the acetylene reduction assay underestimates N<sub>2</sub> fixation by inhibiting diazotrophs sensitive to C<sub>2</sub>H<sub>2</sub>. Aerobic methanotrophy was also inhibited by 1% C<sub>2</sub>H<sub>2</sub>. Comparison of the phylogenetic composition of *nifH* DNA and cDNA amplicon sequences and *nifH* genes in metagenomes and metatranscriptomes from fresh peat sampled at the S1 bog revealed notable differences between primer- vs. omics-based approaches, as well as DNA vs. cDNA sequences. Metatranscriptomes from surface peat were dominated by archaeal *nifH* sequences most similar to *Methanosarcinales*, whereas metagenomes were dominated by nitrogenase paralogs. *In silico* analysis of *nifH* primers previously used in peatland studies revealed multiple mismatches to methanogenic archaeal *nifH* genes. This study suggests that methanogenic archaea may be important soil diazotrophs that have gone undetected due to a combination of C<sub>2</sub>H<sub>2</sub> inhibition during ARA measurements and lack of amplification by common *nifH* primers.

# Early Career Abstracts

## **A geospatial data framework for assessing circumarctic-scale permafrost carbon vulnerability based on observations, experiments and modeling**

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A large amount of organic carbon stored in permafrost soils across the high latitudes is vulnerable to thaw, decomposition and release to the atmosphere as a result of climate warming. This process is anticipated to be a significant positive feedback on future radiative forcing from terrestrial ecosystems to the Earth's climate system. Here, we describe the development of a geospatial data synthesis and analysis framework designed to characterize permafrost carbon vulnerability across the northern high-latitudes. The broadly-defined regional classification is based on a circumarctic spatial representation of the major environmental controls on a) the rate and extent of permafrost degradation and thaw, b) the quantity and quality of soil organic matter stocks, and c) the form of permafrost carbon emissions as CO<sub>2</sub> and CH<sub>4</sub>. The framework was developed by integrating existing spatial data layers describing permafrost and ground ice conditions, bioclimatic zones, and topographic and geographic attributes. The resulting Permafrost Regionalization Map (PeRM) is the foundation for synthesis studies on permafrost carbon vulnerability, including data representativeness, up-scaling and gap analysis along with model-data integration and benchmarking.

The utility of the PeRM framework is demonstrated here through areal density analysis and spatial summaries of existing data collections describing the fundamental components of permafrost carbon vulnerability. We use this framework to describe the spatial representativeness and variability in measurements within and across PeRM regions using observational data sets describing active layer thickness, soil pedons and carbon storage, long-term incubations for carbon turnover rates, and site-level monitoring of CO<sub>2</sub> and CH<sub>4</sub> fluxes from arctic tundra and boreal forest ecosystems. We then use these regional summaries of the observational data to benchmark the results of a process-based biogeochemical model for its skill in representing the magnitudes and spatial variability in these key indicators. Finally, we are using this framework as a basis for higher-resolution mapping of key regions of particular vulnerability to both press (active layer thickening) and pulse (thermokarst development) disturbances, which is guiding on-going research toward characterizing permafrost degradation and associated vegetation changes through multi-scale remote sensing. Overall, this work provides a critical bridge between the abundant but disordered observational and experimental data collections and the development of higher-complexity process representation of the permafrost carbon feedback in geospatial modeling frameworks.

## Multi-system Analysis of Microbial Biofilms

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Examination of natural and engineered environments reveals that the majority of microorganisms live in structured biofilms communities. Biofilms are comprised of microbial cells and an extracellular polymeric substance (EPS) matrix that supports microbial interactions and biogeochemical reactions including extracellular electron transfer (EET). Copious amounts of EPS and EET proteins are co-localized during microbial metal reduction. Their association with nanoparticulate reduced metal suggested that EPS may play key roles in local biogeochemical reactions in subsurface environments.

We employed a multi-faceted approach to determine the composition of biofilm EPS using X-ray and infrared (IR) microimaging techniques combined with electron microscopy and mass spectrometry imaging. The result is a spatially resolved chemical image of a biofilm community. X-ray microtomography produced images of hydrated biofilms to reveal the complex internal microstructure. To investigate the micrometer- to nanometer-scale chemical signatures of biofilms, a cryo-sample preparation technique produced ultrathin biofilm sections for x-ray and IR microimaging. We mapped the unique carbon signatures of biological molecules and found distinct heterogeneities between the cell surface and the EPS matrix. Concurrent with these studies, we produced high-megapixel datasets with IR spectral data showing the locations of key biofilm components (*i.e.*, proteins, sugars, lipids). The spatially resolved IR results were corroborated with bulk IR chemical data.

*In situ* imaging was conducted using a vacuum compatible microfluidic reactor for biofilm growth, confocal laser scanning microscopy analysis, and liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS) imaging. Depth profile sputtering of materials resulted in a layer-by-layer, spatially-resolved live biofilm image. We generated two-dimensional (2D) images of biofilms at their surface attachment interface and detected characteristic fatty acid (FA) fragments. 2D images were reconstructed to visualize three-dimensional (3D) images of hydrated biofilm elucidating a depth-resolved, spatial heterogeneity of key FA components in biofilms and near the biofilm-attachment interface. In particular, C12 and to a lesser degree, C16 FAs were localized throughout the biofilm depth profile while C15 FAs localized deeper into the biofilm. The observed FAs are being further investigated as key factors for how biofilms attach to mineral surfaces using the microfluidic platform.

The integration of the multiscale structural studies and *in situ* imaging of biofilm chemistry provides detailed, high-resolution chemical images of biofilms that will help us to better understand how a biofilm community influences local biogeochemical reactions in subsurface environments.

This work was funded by a U.S. DOE Office of Science Early Career Research Program Award (DOE National Laboratory Announcement 10-395).

River bank erosion transfers sediment, particulate carbon and particulate-bound nutrients from floodplains to rivers. River bank accretion and overbank sedimentation control the flux of these materials in the reverse direction. These fluxes, between rivers and floodplains, strongly influences carbon cycling on floodplains and in rivers, and control the timing, magnitude, and composition of riverine biogeochemical inputs to the coastal ocean. Neither these fluxes nor the dynamics that control them are presently represented in regional or global climate models. As the start of a global analysis to quantify and parameterize river-floodplain exchange rates we present a pan-arctic assessment of river systems draining permafrost-dominated watershed. These systems are of particular interests because of the high sensitivity of permafrost areas to climate change, and the uncertainty associated with the impact of climate change on the fate of carbon in these areas. Using Landsat acquired imagery, we quantified areal and linear rates of river bank erosion and accretion along 6 major arctic rivers. Several smaller rivers systems were also analyzed using aerial photographs and high-resolution satellite imagery. This quantification aims to: 1) develop a predictive framework for river-floodplain exchanges and; 2) quantify the influence of permafrost on river dynamics. We examine the relationship between erosion rates and local and watershed-scale parameters. Local parameters include river width, slope and climate. At the watershed-scale we examined drainage area, basin relief, mean basin slope, climatic variables, vegetation, and soil types. The correlations between these parameters and erosion and accretion rates, as well as future comparisons of these correlations at different climatic and ecologic regimes, will aid in representing these processes in regional or global climate models.

# **Computational Bayesian Framework for Quantification and Reduction of Predictive Uncertainty in Climate Modeling and Groundwater Reactive Transport Modeling**

DOE Early Career Award DE-SC0008272  
Subsurface Biogeochemical Research Program

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In the first two years of the project, we have developed a computational Bayesian framework for uncertainty quantification and reduction in environmental modeling. The framework is mathematically and computationally general, and can be applied to a wide range of environmental problems.

In the third year of the project, we have applied the computational Bayesian framework to both climate change modeling and subsurface reactive transport modeling. The application to climate change modeling is focused on understanding the mechanisms of soil microbial respiration behind the Birch effect, i.e., pulsed wetting causes a dramatic increase in soil respiration after a period of drought. We examined five models with different levels of complexity, evolving from an existing four-carbon-pool model to models with additional carbon pools and explicit representations of soil moisture controls on carbon degradation and microbial update rates. By evaluating structural uncertainty of the models, our Bayesian framework identified the best model, and helped gain insights for understanding why the model outperforms the other models. To facilitate the model identification, we developed a new statistical metric called relative model score, which is evaluated using the results of Bayesian computation of the framework. In addition, by considering eight formal likelihood functions for the soil respiration models, we investigated a fundamental question in Bayesian inference, i.e., how the likelihood functions affect the results of Bayesian inference. This analysis provided a number of insights and guidelines for calculating soil respiration models and for improving predictive capability of the models.

The computational Bayesian framework has also been applied to evaluate the data-worth of geophysical, hydraulic, and transport observations for reducing predictive uncertainty. This study was conducted by collaborating with scientists at the Pacific Northwest National Laboratory for the Hanford 300 Area, where a large amount of field data have been collected in the past. A new method has been developed to use ensemble Kalman filter and level set methods for reducing uncertainty in constructing hydrogeological facies. We are conducting research to evaluate this method using the data available at the 300 Area.

We have also continued on theoretical research to develop new sparse grid collocation methods for computationally efficient implementation of the framework. We proposed a new method to construct sparse grid surrogate for system state variables (e.g., hydraulic head and concentration). The new method has been evaluated for a groundwater flow problem, and we will further evaluate the method for reactive transport problems.

# Ameriflux Abstracts

## Full-column Greenhouse Gas Profiles Measured at ARM SGP

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Grant: KP170201

The vertical distributions of CO<sub>2</sub>, CH<sub>4</sub>, and other gases provide important constraints for the determination of terrestrial and ocean sources and sinks of carbon and other biogeochemical processes in the Earth system. Remote sensing from ground-based and satellite-borne platforms require in-situ validation. We report results from a collaborative measurement campaign between the DOE Biological and Environmental Research Program (DOE-BER) and the NOAA Earth System Research Laboratory (NOAA-ESRL) to quantify the vertically resolved distribution of atmospheric carbon-cycle gases (CO<sub>2</sub>, CH<sub>4</sub>, and CO) throughout 99% of the atmospheric column. To accomplish these measurements, a long coiled tube (or AirCore) is lofted to the stratosphere (~ 30km) on a weather balloon, and then collects a vertically resolved sample of air on descent. From 2012-present, we have conducted more than a dozen AirCore flights from the DOE ARM Southern Great Plains Facility in Oklahoma. Comparisons with collocated ARM aircraft measurements show good agreement for the lower half of the atmospheric column. AirCore profiles are also be integrated to evaluate the ground based (TCCON) column-mean CO<sub>2</sub> and CH<sub>4</sub> mixing ratios. In the past year we have also started development of a automated guidance system that is expected to expedite AirCore recovery of the Aircore packages. The expected outcome of this project will be an operational capability providing data that supports key DOE science objectives.

Title: ARM-ACME projects in the SGP and NSA

Abstract: We present airborne (ARM-ACME) observations and analysis of atmospheric trace gases in the Southern Great Plains (SGP) and the North Slope of Alaska (NSA). The goals of this measurement program are to improve understanding of: (a) land-atmosphere carbon exchanges in the SGP and NSA regions; (b) how CO<sub>2</sub>, CH<sub>4</sub> and associated water and energy fluxes influence CO<sub>2</sub> and CH<sub>4</sub> concentrations; (c) how greenhouse gases are transported on continental scales; and (d) investigate the impact of a fast changing climate on the carbon cycle in the NSA. During flights, we measure CO<sub>2</sub>, CH<sub>4</sub> and meteorological data continuously and collect flasks for a rich suite of additional gases: CO, N<sub>2</sub>O, <sup>13</sup>CO<sub>2</sub>, <sup>14</sup>CO<sub>2</sub>, carbonyl sulfide (COS), and many trace hydrocarbon species. The main objectives of these weekly flights are to quantify trends and variability in atmospheric concentrations of CO<sub>2</sub>, CH<sub>4</sub>, and other greenhouse gases in North America and to improve understanding and modeling of boundary layer - free troposphere exchange dynamics.

## AmeriFlux Carbon Flux Data Processing and Management

PI – Margaret Torn

coPI - Gilberto Pastorello, Cristina Poindexter, Deb Agarwal, Boris Faybishenko, Marty Humphrey, Norm Beekwilder, Tom Boden, Dario Papale,

The AmeriFlux network gathers, curates, and publishes data collected by independently managed field sites, measuring concentrations and fluxes of carbon, water, and energy across the Americas. The data are processed into fluxes, quality controlled, and sent to the network for publication. After the initial data quality control, these data go through a series of post-processing steps to generate derived and value-added data products. To increase the network-wide data consistency, a new in-depth validity check approach has been developed and applied to identify different types of explicit and implicit errors and omissions in specific data flux measurements. This approach is based on detecting the explicit and implicit types of errors. Corrections are carried out in close collaboration with the tower teams. The flux processing pipeline involves two Ustar threshold calculation approaches, namely the Moving Point Test (MPT) and the Change Point Detection (CPD) approaches. An ensemble of Ustar thresholds are generated and used for Ustar filtering as well as uncertainty estimation. Gap-filling of micro-meteorological variables uses a combination of the Marginal Distribution Sampling (MDS) method for shorter gaps and, downscaled data based on the ERA Interim data products for longer gaps. Two methods are used to gap-fill the NEE and energy fluxes: the first based on the MDS method and the second based on Artificial Neural Networks (ANN). Partitioning of NEE into ecosystem respiration and gross primary production (GPP uses two methods: one based on nighttime data and another in daytime data.

In order to enhance data synthesis, land-model evaluation, and other multi-site data applications, efforts are underway to harmonize data and metadata formats within FLUXNET, in close collaboration among AmeriFlux, the European ICOS, and other regional networks. The formats are being implemented for AmeriFlux, ICOS, and FLUXNET, as well as their new releases of standardized sets of flux data products (featuring gap-filling, GPP/respiration partitioning, and uncertainty assessments products). One of the major revisions was to the BADM (Biological, Ancillary, and Disturbance Metadata) protocols. The updates include structure and variable changes to address new developments in data collection related to flux towers and facilitate two-way data sharing. New variables and an extensive addition to the vocabularies used to describe BADM templates allow for a more flexible and comprehensible coverage of field sites and the data collection methods and results.

This presentation will include typical examples of the AmeriFlux carbon data processing and management, illustrating how the developed approach can be used to: (a) combine different types of data into a consistent and reproducible processing pipeline, (b) create a new release of the AmeriFlux and FLUXNET data products, and (c) design the data sharing portal to support users.

## **The AmeriFlux Management Project: Overview**

Margaret Torn (mstorn@lbl.gov) - Berkeley Lab (PI), Dennis Baldocchi, UC Berkeley; Deb Agarwal, Berkeley Lab; Sebastien Biraud, Berkeley Lab; (Co-PIs).

AmeriFlux is a network of more than 100 sites using Eddy Covariance towers to measure ecosystem CO<sub>2</sub>, water, and energy fluxes across the Americas. The DOE AmeriFlux Management Project ([ameriflux.lbl.gov](http://ameriflux.lbl.gov)) serves a broad community of flux sites and data users. This poster will present some of the main resources and new highlights, including a new rapid-response flux system that can be loaned to sites that have an unanticipated yet valuable research opportunity; the long-term AmeriFlux Core Sites; and technical QA/QC offerings like calibration gases and site visits.

# **EMSL**

# **Abstracts**

## Novel analysis approach and new insights from UHR MS of soil organic matter

Malak M Tfaily, Nikola Tolic, E Robby Robison, Ljiljana Pasa-Tolic and Nancy J Hess

### **Abstract:**

The focus on ecosystem stress and climate change is currently relevant as researchers and policymakers strive to understand the feedbacks between soil C dynamics and climate change. Successful development of molecular profiles that link soil microbiology with soil carbon (C) to ascertain soil vulnerability and resilience to climate change would have great impact on assessments of soil ecosystems in response to climate change. Additionally, a limited understanding of the molecular composition of SOM prohibits the ability to routinely decipher chemical processes within soil and predict how terrestrial C fluxes will respond to changing climatic conditions. The use of ultra-high resolution Fourier transform ion cyclotron resonance mass spectrometry (UHR FTICR-MS) has enabled the examination of organic molecules, directly from soil matrices, with ultrahigh mass resolution and sub-ppm mass accuracy. In this study, EMSL's extensive expertise and capabilities in UHR MS proteomics were leveraged to develop extraction protocols for the characterization of carbon compounds in SOM, thereby providing the chemical and structural detail needed to develop mechanistic descriptions of soil carbon flow processes. In particular, we present a new extraction approach for more representative characterization of SOM thereby providing the necessary details needed to develop mechanistic descriptions of soil C flow processes. Using statistical approaches to analyze the mass spectrum we have been able to differentiate closely related soils prior to assigning chemical formula. Using molecular assignments we identify thousands of individual compounds in complex soil mixtures with a wide range of C content representing diverse ecosystems within the USA. We found that the yield of the chemical extraction was dependent on (1) the type of solvent used and its polarity, (2) sample-to-solvent ratios and (3) the chemical and physical nature of the samples including their origins. We have developed a sequential extraction protocol that permits sampling diverse classes of organic compounds while minimizing ionization competition in ICR cell. Using this approach we have identified possible chemical reactions relating classes of organic molecules that reflect abiotic and biotic processes which impact soil carbon composition. Examples of this approach will be presented from field studies of simulated climate change, vegetation restoration of long-term agricultural fields, and natural fire events.

# **SBIR**

# **Abstracts**

## Cloud based predictive assimilation framework for subsurface site management

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Subsurface system behavior is driven and controlled by the interplay of physical, chemical, and biological processes which occur at multiple temporal and spatial scales. Timely predictive understanding of this behavior is needed both for scientific purposes and for effective system management – whether this is for subsurface remediation, ecosystem services optimization, or water and soil management. Current approaches to develop system understanding typically use desktop based manual approaches for data reduction, numerical modeling and data visualization. Such approaches have fundamental limitations in how timely, effectively and reproducibly they can provide the required understanding.

Under a DOE SBR funded SBIR Subsurface Insights is implementing a cloud based predictive assimilation framework (PAF) which automatically ingests, quality controls and stores heterogeneous subsurface data and processes these data using different inversion and modeling codes to provide information on the current state and evolution of the subsurface system. PAF is implemented as a cloud based software application which has five components: (1) data acquisition, (2) data management, (3) data assimilation and processing, (4) visualization and result deliver and (5) orchestration. Data is associated with discrete projects. Users are associated with one or more projects and different project specific access levels. Users interact with PAF through a standard browser. Modularity of the system is achieved by implementing each core capability of PAF (such as data visualization, user configuration and control, electrical geophysical monitoring and email/SMS alerts on datastreams) as a SPA (Single Page Application). This approach allows for relative simple system development and maintenance. PAF is implemented server side as a modular Zend Framework 2 Web application, supported by different components such as Doctrine (a PHP library for automated object mapping), automated parsers, public data harvesters (e.g. waterlevel and weather data), data standards and python workflows. The client side of PAF is mainly Javascript, which provides for responsive capabilities. Data in PAF is exposed through webservices which allows for easy integration of PAF components in 3<sup>rd</sup> party applications as well as in planned mobile applications. Data assimilation capabilities for PAF are being developed in collaboration with scientists from the LBNL SFA2. PAF is being validated and tested using hydrological, geochemical and geophysical data from the Rifle field site.

# DOE Lab Abstracts

## **Interoperable Design of Extreme-scale Application Software (IDEAS): Software development methodologies that enhance scientific productivity**

Mike Heroux<sup>1</sup>, Lois Curfman McInnes<sup>2</sup>, David Moulton<sup>3</sup>, David Bernholdt<sup>4</sup>, Hans Johansen<sup>5</sup>

While extreme-scale computational architectures provide unprecedented resources for scientific discovery, the community faces daunting productivity challenges for parallel application development. Difficulties include increasing complexity of algorithms and computer science techniques required in multiscale and multiphysics applications, the imperative of portable performance in the midst of dramatic and disruptive architectural changes on the path to exascale, the realities of large legacy code bases, and human factors arising in distributed multidisciplinary research teams. At the same time, software engineering and productivity approaches, processes, and tools have matured substantially in recent years and offer compelling capabilities that we need to understand, adapt, and adopt for scientific software development environments.

The project on **Interoperable Design of Extreme-Scale Application Software (IDEAS, <http://www.ideas-productivity.org>)** aims to qualitatively change the culture of extreme-scale computational science and to provide a foundation that enables transformative next-generation predictive science and decision support. IDEAS motivation is to increase software development productivity—a key aspect of overall scientific productivity—through an interdisciplinary and agile approach to creating extreme-scale scientific software, where modern software engineering tools, practices, and processes will improve software developer productivity, and applications will be constructed quickly and efficiently using components, libraries, and frameworks.

This poster will provide an overview of four complementary focus areas:

**IDEAS Use Cases:** IDEAS work is driven by two important BER use cases: climate impacts on the upper Colorado river system and hydrology and soil carbon dynamics of the Arctic tundra. These use cases will demonstrate the scientific productivity gains that are possible with a software ecosystem that enables scientists to engage effectively in their areas of expertise, while readily employing cutting-edge numerical algorithms and software developed by ASCR research teams (see poster by Moulton et al. for overview of the Use Cases)

**IDEAS xSDK:** The IDEAS Project involves members from five major DOE library products: Chombo, hypre, PETSc, SuperLU and Trilinos. A major deliverable of IDEAS is the Extreme-scale Scientific Software Development Kit (xSDK), which will provide an interoperability layer that will enable easy installation and usage of the IDEAS libraries.

**IDEAS HowTo:** In addition to xSDK development and other software efforts to address the IDEAS use cases, IDEAS will focus on methodologies (“howto” content) to cultivate best practices, processes, and tools for improved scientific software development.

**IDEAS Outreach:** The final piece of IDEAS is outreach and collaboration with the broader computational science community, which is also facing similar challenges and opportunities for improving productivity.

(1) Sandia National Laboratories, (2) Argonne National Laboratory, (3) Los Alamos National Laboratory, (4) Oak Ridge National Laboratory, (5) Lawrence Berkeley National Laboratory

## Environmental Systems Science Use Cases Drive Requirements for Community-Based Software Development

David Moulton<sup>1</sup>, Carl Steefel<sup>2</sup>, Scott Painter<sup>3</sup>, Tim Scheibe<sup>4</sup>, Reed Maxwell<sup>5</sup>, Ethan Coon<sup>1</sup>, Glenn Hammond<sup>6</sup>, Xiaofan Yang<sup>4</sup>

The need to understand and predict climate impacts and feedbacks in terrestrial systems is driving a trend toward more mechanistic representations of coupled aboveground and belowground processes, thus creating challenges in multiscale and multiphysics modeling. The *Interoperable Design of Extreme-Scale Application Software* (IDEAS) project is exploring new community-based approaches to software development that will lead to application codes that are more accessible to developers and users, enhancing their productivity (see IDEAS overview poster by McInnes et al.). To guide this work in IDEAS, two Use Cases have been selected that address scientific questions for existing Environmental Systems Science application projects, as well as exercise components of established and new codes.

Use Case 1 focuses on the East River Watershed within the Upper Colorado River Basin, a snowmelt dominated, 750 km<sup>2</sup> high elevation headwaters catchment that is under study as part of LBNL's Genomes to Watershed Scientific Focus Area (SFA). The LBNL SFA will investigate how climate change impacts biogeochemical cycling in a watershed mediated by hydrology and the distribution and function of dynamic microbial communities. This Use Case considers a portion of the lower East River dominated by a broad flood plain in which stream meanders and associated hyporheic zone flow contribute to carbon cycling. Resolving redox and other geochemical gradients at scales < 1 meter, while upscaling these results to the larger (5km) scale river system, is the computational challenge that will drive advances in interoperability and performance in the Amanzi/ATS, ParFlow-Crunch and PFLOTRAN codes. Also, IDEAS will explore a multiscale model coupling framework in a similar setting under the PNNL SFA (see poster by Scheibe et al.).

Use Case 2 links to the NGEE Arctic program, focusing on software interoperability and productivity enhancements to enable more realistic simulations of permafrost thaw and active layer dynamics in polygonal patterned ground at the Barrow Environmental Observatory. The IDEAS project will combine fine-scale simulations of permafrost thermal hydrology using the Arctic Terrestrial Simulator (ATS) with PFLOTRAN's geochemistry engine through the chemistry interface library, Alquimia. To demonstrate reuse of physics components in new applications, IDEAS is extending ATS's fine-scale modeling capabilities to the intermediate scale through the use of mesh and model domain abstractions. Here, thermal hydrology will be simulated on a set of independent 1D columns, where each column represents an ice-wedge polygon. Those columns will be coupled to each other laterally through 2D simulations of overland flow including dynamic topography.

(1) Los Alamos National Laboratory (2) Lawrence Berkeley National Laboratory (3) Oak Ridge National Laboratory (4) Pacific Northwest National Laboratory (5) Colorado School of Mines (6) Sandia National Laboratory

## CLM-Agni-Akuna Integration Demonstration: A Community Platform for Uncertainty Quantification

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The U.S. Department of Energy (DOE) office of Environmental Management (EM) is investing in development of a numerical modeling toolset called ASCEM (Advanced Simulation Capability for Environmental Management) to support modeling analyses at legacy waste sites. ASCEM is an open source and modular computing framework for predicting contaminant fate and transport in natural and engineered systems. The ASCEM toolset includes a data management and user interface platform (called Akuna) integrated with a simulation controller (called Agni), which work together to develop and execute simulations of subsurface flow and reactive transport using a high-performance computing multi-process simulator (called Amanzi). The Akuna-Agni platform provides the user interface and toolsets for managing workflows, including model development starting with definition of the conceptual model, management of data and metadata for model input, sensitivity analysis, model calibration and uncertainty analysis, model execution on diverse computational platforms, and processing of model output, including visualization.

Development of the ASCEM toolset has incorporated scientific advances developed by the Subsurface Biogeochemical Research (SBR) program, and SBR program managers and investigators have been actively involved in the ASCEM project since its inception. ASCEM components have been developed using advanced software development methodologies, with an emphasis on modularity, portability and extensibility to maximize utility by a broad user community. Although the ASCEM project is focused on the Amanzi subsurface reactive transport simulator, the Akuna-Agni platform can be customized to link to other simulation tools, facilitating reuse of system components such as data management, visualization, uncertainty quantification, sensitivity analyses, and parameter estimation that are useful to a wide range of earth systems modeling efforts.

This poster describes a collaborative demonstration project undertaken by members of the PNNL and LBNL SBR Scientific Focus Area projects and other key collaborators at those two institutions. We have customized the Akuna-Agni platform to integrate the Community Land Model (CLM) simulator, and are applying this system to several research sites to demonstrate its capabilities. Completed demonstrations include 1) 1D CLM simulations of the NGEE-Arctic site, with sensitivity analysis performed on several soil parameters (e.g., organic content, percent clay and sand), and 2) 1D CLM simulations of the ARM Southern Great Plains (SGP) site, with sensitivity analysis of ten parameters (with results compared to a previous publication using a different method) and application of the parameter estimation toolset. We are also working toward demonstrations of 3D CLM simulations at the NGEE-Arctic and Hanford 300 Area sites.

## **Interactions between plant physiology and atmospheric chemistry as a part of the GoAmazon 2014/15 Terrestrial Ecosystem Collaborative Project (Geco)**

Kolby Jardine<sup>1</sup>, Antonio Manzi<sup>2</sup>, Jennifer Holm<sup>1</sup>, Margaret Torn<sup>1</sup>, Niro Higuchi<sup>2</sup>, Jeffrey Chambers<sup>1</sup>

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Emissions of biogenic volatile organic compounds (BVOCs) from tropical forests play central roles in atmospheric processes by fueling atmospheric chemistry resulting in modified aerosol and cloud lifecycles and their associated feedbacks with the terrestrial biosphere. However, the identities of tropical BVOCs, their biological and environmental controls, and functions within plants and ecosystems remain highly uncertain. In addition, the accurate representation of atmospheric and biological processes associated with BVOCs within Earth System Models including the Community Land Model requires a tight connection between observational and modeling efforts. As part of the DOE ARM program's GoAmazon 2014/15 campaign, extensive field and laboratory observations of BVOCs are being conducted in the central Amazon together with model development aimed at improving the representation of BVOCs in the Community Land Model. Here we report the results of our ongoing Terrestrial Ecosystem Science (TES) activities at the National Institute of Amazon Research (INPA) in Manaus, Brazil, the ZF2 forest reserve in the central Amazon, and Lawrence Berkeley National Laboratory. Among the results of the research is new evidence for the importance of BVOCs in protecting plants from oxidative stress under elevated temperatures highlighting the need to model allocation of carbon to BVOCs to protect against the damaging effects during environmental extremes. We provide a brief overview of the results recently described in nine papers published in international journals including *Plant Physiology*, *Plant Cell and Environment*, *Atmospheric Chemistry and Physics*, *Global Biogeochemical Cycles*, and *Geophysical Research Letters* as well as current progress in ongoing research in the last year of the GoAmazon project.

# Mechanisms and traits associated with plant survival and mortality during drought

Sanna Sevanto, Chonggang Xu, Nate McDowell

Earth and Environmental Sciences Division, Los Alamos National Laboratory

Drought-related, continental-scale forest mortality events have been observed with increasing frequency during the past 20 years. In the future, higher frequency of droughts is predicted to be accompanied with increasing temperatures that could lead to large-scale forest mortality. At Los Alamos National Laboratory we have built new capabilities to study how different traits in plant anatomy and physiology influence plant performance and survival/mortality during drought and elevated temperatures. By combining studies on microfluidics inside a tree with detailed anatomical studies and tree- and ecosystem-scale experiments we aim at understanding the fundamental connections between plant traits and plant mortality, and using this information for improving predictions of future vegetation changes in DOE-sponsored Earth System Models. At the microfluidics scale we use 3D x-ray tomography, combined with neutron radiography and Nuclear Magnetic Resonance techniques to reveal how anatomy of different species affects their water use and vulnerability to hydraulic failure or carbon starvation. With plant-scale manipulation experiments we measure key parameters determining the vulnerability of plant hydraulics and carbon transport systems during drought, and with ecosystem-scale climate-manipulation experiments of mature trees we detect how these traits manifest during drought and under elevated temperature.

Our results show trait differences in desiccation tolerant and desiccation avoiding plants that influence the internal water and carbon cycling, and may have implications to maintaining hydraulic connection with the soil during drought. But, interestingly no theoretically predicted anatomical differences that could explain the observed differences in vulnerability to hydraulic failure of these species were found. Combined with observations of plant adaptations to dry growth conditions, these results indicate that drought mortality of both desiccation tolerant and desiccation avoiding plants is influenced jointly by carbohydrates storage and transport dynamics.

## Utilization and transformation of terrestrial carbon in northern landscapes

Karis McFarlane, Jennifer Pett-Ridge, Gavin McNicol, Xavier Mayali, Mike Singleton, Ate Visser, Heather Throckmorton, Paul Hanson and Tom Guilderson

High-latitude terrestrial systems are particularly vulnerable to climate change and present significant uncertainties to predictions of future sources and sinks for carbon on land. We are investigating carbon utilization and transformation in northern landscapes at two DOE sites, NGEA Arctic and SPRUCE. Production and loss of dissolved organic carbon (DOC) is an important mechanism for ecosystem carbon loss that results in considerable export off the Arctic landscape, reducing or eliminating carbon sinks. At the NGEA-Arctic site (Barrow, Alaska), we have determined the  $^{14}\text{C}$ -age and chemistry of DOC from surface and peat pore water from 17 drainages sampled in July and September 2013. DOC ages ranged from modern to ~5600 years and increased with depth, from July to September, and with increasing DOC, DIC, and DON concentrations. In September, sites with older DOC in deep pore waters also had highly depleted  $\delta^{13}\text{C}$  of dissolved  $\text{CH}_4$ , suggesting a link between DOC source and methanogenesis pathways. Spectral analysis suggested a shift in DOC chemistry with depth and sampling month, but we found little evidence for a connection between DOC age and chemistry. To elucidate the response of boreal wetlands to changing climate, we are collaborating with SPRUCE to identify 1) microbial communities producing and consuming  $\text{CH}_4$  and interactions with N-fixers, 2) the source of carbon used for production of  $\text{CO}_2$  and  $\text{CH}_4$ , and 3) how these respond to ecosystem warming treatments. Isotopic analysis of  $\text{CO}_2$  and  $\text{CH}_4$  from surface chambers indicate that the source for the emitted carbon is mostly recent, with most  $^{14}\text{C}$  values between 30 and 50‰ for  $\text{CO}_2$  (i.e., carbon that was photosynthetically fixed in the last decade) and 50- 90‰ for  $\text{CH}_4$  (i.e., carbon that was photosynthetically a decade or two ago). Respired  $^{14}\text{CO}_2$  values decreased during the growing season, to values consistent with current year photosynthate.  $^{14}\text{CH}_4$  followed a similar trend over the growing season, but was more variable earlier in the summer when fluxes were small. While deep peat heating did occur at SPRUCE in 2014, it appears that surface C fluxes were more influenced by seasonal surface effects. This suggests that under the current climate, microbes shift towards increased use of new photosynthates over the growing season and, on average, emitted  $\text{CH}_4$  is roughly a decade older than emitted  $\text{CO}_2$ . These results illustrate the critical importance of future  $^{14}\text{C}$  measurements in isolating ecosystem patterns and processes that contribute to terrestrial carbon balance across the landscape.

Acknowledgements: Allison Gill, Michelle Predi, Jeff Chanton Robert Nettles, Mary Whelan, Joel Kostka, Brent Newman, Jeff Heikoop

## **Title: Pore- to Core-Scale Research to Inform Ecosystem-Scale Soil C Biogeochemistry**

Program: Terrestrial Ecosystem Science Program

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The spatial separation of substrate, microbes, and extracellular activity is an important mechanism of soil organic carbon (SOC) protection in soils, and one that is difficult to represent in predictive models at any scale. Macropore networks and their connectivity control microbial access to physically protected C in soils. Under conditions of partial to full water saturation, potentially labile compounds can desorb and diffuse from micropore domains to macropore networks accessible to microorganisms. Therefore, the quality of the SOC in pore waters held with different tensions is a key characteristic needed to differentiate physical and chemical SOC protection mechanisms. The decomposability of this C is needed to determine its potential contribution to net GHG fluxes as the protection mechanism breaks down through changing local environmental conditions.

We have studied intact soil cores collected from the Disney Wilderness Preserve, FL (DWP). Water dynamics in this system, particularly water table rise and fall, appear to be a strong control on the emissions of C-gases and the persistence of soil organic matter. Soils at DWP are dominated by sandy textures, and depending on local topographic position show moderate to high levels of SOM accumulation at the surface. Samples of soil pore water held at two different water tensions were collected from three continuous-depth DWP soil cores (0-30, 30-60, and 60-90 cm), from three transect locations (dry, intermittently wet, and wet). The more tightly held pore waters (500 mb) had significantly more condensed hydrocarbons and tannins compared to the more loosely held water (15 mb), which had significantly more lipids. These differences were consistent for all three transect positions, and all three soil depths. These pore waters were then used as growth substrates for cultivation of selected bacteria (*Streptomyces cellulosa*, *Cellvibrio japonicus*) and fungi (*Trichoderma reesei*). For all organisms, significantly more CO<sub>2</sub> was respired from the higher-tension pore waters characterized by the more complex C compounds. If mobilized, currently-protected SOC would become biologically available and contribute to greenhouse gas fluxes to the atmosphere.

## **Integrating models of greenhouse gas production from soils at multiple scales**

Ben Bond-Lamberty, Todd-Brown, Chongxuan Liu, Zhifeng Yan, and Vanessa Bailey  
March 3, 2015

The mobilization, decomposition, and respiration of soil carbon represents the second largest greenhouse gas (GHG) fluxes of the terrestrial biosphere, and is critical to understand across pore to core to ecosystem scales. This poster integrates recent PNNL research on how models can effectively simulate the interaction of temperature, water, and soil carbon processes at multiple scales.

At pore scales, reactive transport models (RTM) for simulating biogeochemical reaction network and kinetics under variable water saturation conditions are being developed in the framework of our previously developed unified multi-scale modeling. The RTMs are being used to evaluate how pore-scale hydrological connectivity affects soil organic matter degradation and GHG release in soils, and to derive functional relationship between GHG flux and water saturation at the macroscopic scale.

At larger scales, models typically have use multiple pools governed by first-order kinetics to simulate GHG soil production, and historically have been parameterized via expert tuning. Modern data integration techniques, however, can be used to robustly and reproducibly integrate data from laboratory and field experiments with predictive models. This not only provides formal parameterizations, but also quantifies the level of support for competing model structures provided by the data; when combined with *a priori* scientific understanding, this can be used to select the ‘best’ model at a particular temporal or spatial scale. In a sample analysis of this type, we consider models with varying number soil carbon pools and connections between those pools, and use data from soil incubation experiments encompassing a range of soil types and durations.

# **Next Generation Ecosystem Experiments (NGEE) Arctic Abstracts**

## The Role of Landscape Structure on Arctic Ecosystem Response

DOE BER Terrestrial Ecosystem Science Program

Authors: Cathy J. Wilson, LANL; Larry Hinzman, UAF; Susan S. Hubbard, LBNL; PI Stan Wullschleger, ORNL.

A fundamental goal of the Next-Generation Ecosystem Experiments (NGEE-Arctic) project is to improve climate prediction through process understanding and representation of that knowledge in Earth System models. Geomorphological units, including thaw lakes, drained thaw lake basins, and ice-rich polygonal ground provide the organizing framework for our scaling approach for the coastal plains of the North Slope of Alaska. Process studies and observations have been undertaken in and near the Barrow Environmental Observatory, BEO, across nested scales to understand and quantify the interactions between geomorphic landscape features, hydrology, soil temperature, biogeochemistry, vegetation patterns, and energy exchange in order to initialize and evaluate a suite of models within the NGEE hierarchical modeling framework. In-situ, ground based geophysical, airborne and satellite based observations are carried out across gradients of micro-topographic features (polygon rims, centers and troughs) and polygon types (high centered, low centered and transitional) that are nested within a landscape comprised of drained thaw lake basins of varying ages and structures. Our studies are showing clear correlations between geomorphic features, and the dynamics of soil moisture, soil temperature and surface inundation patterns across the landscape, as well as soil biogeochemistry, vegetation patterns, and carbon and energy fluxes. Our data and findings are now being used to initialize and evaluate fine, intermediate and global scale models which will be soon be used to simulate the evolution of a warming and thawing Arctic landscape and its feedbacks to the global climate system.

Title: Topographic controls on scaling of hydrologic and thermal processes in polygonal ground features of an Arctic ecosystem

Authors: Gautam Bisht<sup>1</sup>, William J. Riley<sup>1</sup> and Haruko Wainwright<sup>1</sup>

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Abstract

Arctic and sub-Arctic soils currently contain approximately 1700 billion metric tones of frozen organic carbon, approximately 200 times current annual anthropogenic emissions. This carbon is vulnerable to release to the atmosphere as CO<sub>2</sub> and CH<sub>4</sub> as high-latitude temperatures increase due to climate change. Microtopographic features, such as polygonal ground, are characteristic sources of landscape heterogeneity in the Alaskan Arctic coastal plain. Polygonal ground structures, with high or low centers, influence the distribution of snow depth, thereby impacting the energy balance, biogeochemical dynamics, vegetation communities, and carbon releases from the subsurface. In spite of the importance of heterogeneous snowpack on local hydrologic and thermal processes, they are not explicitly accounted for in land surface models.

In this study, we develop a snow redistribution algorithm, which accounts for microtopography, in the Community Land Model (CLM4.5). We perform simulations for four sites in Barrow, AK at multiple horizontal resolutions across several years with imposed soil heterogeneity. Results indicate that heterogeneous distribution of snow, accumulated during winter months, has a strong influence on spatial distribution of active layer depth and surface energy fluxes during the summer season. In winter, soil temperature variance ( $\sigma_T^2$ ) exhibits a non-linear relationship with spatial scale. Coarse resolution simulations under predict  $\sigma_T^2$  when compared to the spatial average of the fine resolution simulations. Lastly, we investigate the role of 3D versus 1D subsurface thermal processes by including lateral subsurface thermal transport in CLM4.5. The 3D process representation leads to lower winter soil temperature variability when compared to 1D simulations.

# Multi-scale modeling of permafrost freeze-thaw dynamics in polygonal tundra

Jitendra Kumar<sup>1</sup>, Nathan Collier<sup>1</sup>, Gautam Bisht<sup>2</sup>, Peter Thornton<sup>1</sup>

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## Abstract

Organic carbon rich Arctic ecosystem is highly sensitive to the climate change induced warming which may lead to release of carbon in form of  $CO_2$  and  $CH_4$  from previously frozen soils. Arctic ecosystem consist of complex and interconnected hydrologic, thermal, biogeochemical, geomorphic and vegetation processes. Local to regional scale eco-hydrologic processes are often influenced by micro-topographic variations in the topographically and geomorphologically complex landscape.

Increasing temperatures trigger disturbance in the thermal balance of permafrost freeze-thaw dynamics which propagates through the system via complex process interactions and feedbacks. Modeling of the permafrost freeze-thaw dynamics is key to understand the fate and evolution of the landscape in the warming climate. The Department of Energy's Next Generation Ecosystem Experiments (NGEE–Arctic) project is developing a multi-scale modeling framework to model eco-hydrologic processes in the Arctic ecosystems.

We have developed a finite volume method based model for coupled surface–subsurface mass and energy balance within PFLOTRAN—an open source, state-of-the-art massively parallel subsurface flow and reactive transport code. High resolution 3-D multi-phase thermal model captures the the microtopography and parameterized using field based observations data sets to understand the controls of polygonal tundra microtopography (centers/troughs/ridges) in high-centered/low-centered/transitional polygon landscapes.

Model was applied at NGEE–Arctic field sites at Barrow Environmental Observatory in Alaska. Sub-meter resolution LiDAR based Digital Elevation Model was used to capture the microtopography in high resolution model. Soil hydraulic and thermal properties were parameterized using observations from spatially distributed soil cores. Long term meteorological observations at the sites were used to force the simulations and spatially distributed records of active layer thickness employed to validate and calibrate the model.

Complex non-linear thermal hydrologic processes in heterogeneous Arctic landscape pose numerical and computational challenges. Robust numerical schemes has been developed in scalable parallel PFLOTRAN model for large scale realistic simulations of NGEE–Arctic field sites informed by field and laboratory observations.

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## Conceptualization and Application of Arctic Tundra Landscape Evolution Using the Alaska Thermokarst Model

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Thermokarst topography forms whenever ice-rich permafrost thaws and the ground subsides due to the volume loss when excess ground ice transitions to water. The Alaska Thermokarst Model (ATM) is a large-scale, state-and-transition model designed to simulate transitions between [non-]thermokarst landscape units, or cohorts. The ATM uses a frame-based methodology to track transitions and proportion of cohorts within a 1-km<sup>2</sup> grid cell. In the arctic tundra environment, the ATM tracks thermokarst-related transitions between wetland tundra, graminoid tundra, shrub tundra, and thermokarst lakes. The transition from one cohort to another due to thermokarst processes can take place if thaw reaches ice-rich ground layers either due to pulse disturbance events such as a large precipitation event or fires or due to gradual active layer deepening that eventually results in penetration of the protective layer. The protective layer buffers the ice-rich soils from the land surface and is critical to determine how susceptible an area is to thermokarst degradation. The rate of terrain transition in our model is determined by the ice-content of the soil, the drainage efficiency (or ability of the landscape to store or transport water), and a cumulative probability of thermokarst initiation. Tundra types are allowed to transition from one type to another (ie wetland tundra to a graminoid tundra) under favorable climatic conditions. In this study, we present our conceptualization and initial simulation results from the ATM model for an 1792 km<sup>2</sup> area on the Barrow Peninsula, Alaska. The area selected for simulation is located in a polygonal tundra landscape under varying degrees of thermokarst degradation. The goal of this modeling study is to simulate landscape evolution in response to thermokarst disturbance as a result of climate change.

Importance of considering small-scale polygonal tundra geomorphology in large-scale terrestrial ecosystem models for assessing change in landscape-level carbon balance on the Barrow Peninsula

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Northern permafrost regions are estimated to cover 16% of the global soil area and account for approximately 50% of the global belowground organic carbon pool. However, there are considerable uncertainties regarding the fate of this soil carbon pool with projected climate warming over the next century. In northern Alaska, nearly 65% of the terrestrial surface is composed of polygonal tundra, where geomorphic land cover types (i.e. high-center polygon) disproportionately influence local surface hydrology, plant community composition, nutrient and biogeochemical cycling, over small spatial scales. Due to small-scale (1-100 m) geomorphic spatial heterogeneity of Arctic tundra, and the relatively large (1km<sup>2</sup> - 0.5°) spatial extent in which process-based biogeochemical models used for long-term change determination, it is uncertain which small-scale geomorphic types are critical to consider within a large-scale modeling framework to minimize error associated with simulated spatial and temporal patterns of change. This work evaluates the relative importance of multiple geomorphic types on large-scale modeling assessments, using the terrestrial ecosystem model (DOS-TEM). We parameterize and calibrate this model using data specific to the local climate, vegetation, and soil associated with tundra individual geomorphic types, and extrapolate model results at a 1km<sup>2</sup> resolution across the ~1800 km<sup>2</sup> Barrow Peninsula using a map that describes eight dominant geomorphic tundra types. Next, data for eight geomorphic types (initial) are iteratively simplified based on similar characteristics within a hierarchical cluster analysis, while the model is re-parameterized, re-calibrated, and re-extrapolated using 8, 6, 4, and 3 classes. We evaluate differences between initial and reduced class sizes on changes in landscape-level carbon balance between 1970 and 2100. Preliminary simulations for this region indicated temporal variability in response to carbon and active layer dynamics, specific to tundra geomorphic type, and presents the landscape-level potential error in simulated carbon balance associated with reduced class size.

## **Using fine-scale models to inform next-generation Earth system models**

Authors: Ethan T. Coon, J. David Moulton, Rao Garimella, Adam L. Atchley, Cathy J. Wilson, Dylan Harp (LANL), Scott L. Painter (ORNL)  
PI: Stan D. Wullschleger (ORNL)

Understanding and predicting the impacts of and feedbacks on climate in the terrestrial Arctic is made difficult by two major issues – the extreme complexity of the coupled thermal-hydrological-mechanical-biogeochemical system, and the differences in scale between the coarse scale at which Earth system models run and the fine scale at which physical process descriptions and many field measurements are appropriate. In NGEE Arctic, we have made extensive use of fine-scale models as an integration tool, interpreting existing and new observations at a scale relevant to that observation. In turn, the fine-scale model is used to inform decisions on how to appropriately represent processes in Earth system models.

Here we discuss one of NGEE Arctic's fine-scale simulation capabilities -- the Arctic Terrestrial Simulator (ATS), describing how it can be used as this integration tool and demonstrating ongoing work in fine-scale modeling. We demonstrate how ATS builds on Arcos, a strategy for managing complexity and enabling experimentation with process representation. Arcos enables process-rich modeling capabilities by allowing complexity to be extended incrementally, with testing, validation, and ModEx-driven calibration at each step to build trust in the model. We show a workflow in which remote sensing and field observations are used to develop meshes, inform spatially distributed parameters, and provide input data for simulations. And finally, we show ATS's value as a model experimentation and predictive tool, enabling flexibly configured, process-rich simulations of ecosystems in a variety of dimensions, at a variety of spatial and temporal resolutions, and with a variety of process complexities. As a key component in NGEE Arctic's strategy, we show how application of ATS and fine-scale models to 2 and 3D domains is being used to understand the interplay between micro-topography in ice-wedge polygon landscapes and thermal hydrologic response and its evolution with a warming climate.

## **Geophysics-based Multiscale Characterization of the Arctic Tundra Ecosystem**

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Working within an Arctic ice-wedge polygonal region near Barrow AK, we have developed geophysics-based strategies to estimate the spatially heterogeneous aboveground/belowground ecosystem properties – such as vegetation, soil moisture, soil temperature, thaw depth, soil hydrological and mechanical properties, and greenhouse gas (GHG) fluxes – as well as to understand their interaction and dynamics from the core-scale (~10cm) to the site-scale (~1km). Laboratory core analysis provided new insights into biogeochemical processes and associated geophysical signatures. Freeze-thaw experiments using a soil column were performed to quantify how progression of a thaw front influences biogeochemical and mechanical responses, and the associated electrical signature. Results revealed a significant ‘spring burp’ of GHG at first thaw (also detected in field data), and changes in electrical responses associated with soil mechanical failure, controlling GHG fluxes. Seismic petrophysical studies provided information needed to interpret and validate field seismic imaging of an unfrozen region of saline permafrost. X-ray computed tomography was used to identify the structure of active and permafrost layers, aiding the interpretation of field geophysical data and revealing fine-scale cyrostructures that may play a significant role in gas transport. Core measurements of hydrological, mechanical and electrical properties provided direct information for model parameterization such as hydraulic conductivities.

Field data collection focused on establishing and quantifying the spatiotemporal linkage among various above/belowground properties in high resolution, using spatially extensive remote sensing and surface geophysical data. We developed a nested monitoring strategy, including seasonal campaigns along 500x40 m ‘intensive sampling’ corridors, as well as continuous autonomous monitoring of ecosystem dynamics at high temporal/spatial resolution along a 35 m transect. Continuous monitoring enabled us to visualize a tightly coupled system such as the correlation between the electrical conductivity (sensitive to water content and soil structure) and thawed layer thickening and vegetation development during the growing season. The datasets at the ‘intensive sampling’ corridors were used to develop a ‘functional zone’ approach for integrating multi-type multiscale datasets and for distributing critical land- and subsurface properties over the landscape. A statistical analysis confirmed that polygon types could be regarded as Arctic ecosystem functional zones, capturing the variations in important ecosystem properties (including GHG fluxes). In addition, seismic data provided the properties of deep permafrost units, in particular the vertical and lateral extent of partially frozen soils beneath the surficial ice wedge complex. Together, the geophysics-based acquisition and inversion approaches are providing unique high-resolution information and new insights about the Arctic ecosystem functioning as well as providing information to models - at scales and resolutions useful for predicting terrestrial ecosystem feedbacks to the climate.

## **Integrating Field Measurements in Fine Scale Model Development for Understanding Future Active Layer Thickness Dynamics**

Authors:

Adam L. Atchley, Ethan T. Coon, Scott L. Painter, Dylan Harp, Anna K. Liljedahl, V. E. Romanovsky, Cathy J. Wilson

Projections of active layer thickness (ALT) – the annual maximum depth of soil with above 0°C temperatures – is a proxy for the volume of carbon-rich stores available for decomposition and therefore potential greenhouse gas release into the atmosphere from Arctic tundra. However, projections of ALT in polygonal tundra is challenging due to the complex nature of hydrothermal atmospheric-surface-subsurface interactions in freezing/thawing soil, which then requires extensive calibration to field observations and model refinement to capture the key processes necessary to simulate fine scale thermal hydrology. Soil temperature and snow data from the Barrow Environmental Observatory, Alaska are used to calibrate hydrothermal properties of moss, peat, and mineral soil in the multiphysics Arctic Terrestrial Simulator (ATS) models. When calibration failed to match measured data or produced calibrated parameters that are physically unrealistic, conceptual understanding was reassessed and model structure was refined. This iterative model refinement procedure that cycled between observations and model development (ModEx) was used to create models that simulate ALT in polygonal tundra permafrost environments. Applications of the model are being used to understand the interplay between micro-topography in ice-wedge polygon landscapes and thermal hydrologic response and its evolution with warming climate that then informs how physical characteristic such as peat thickness, saturation, and snow depth influence ALT formation. The calibrated model and increased process understanding was then used to examine the role of subsurface thermal properties on uncertainty in predicted ALT in the year 2100.

## Rates and pathways of permafrost soil organic carbon degradation in Arctic tundra

Ziming Yang,\* Taniya Roy Chowdhury, Stan Wullschleger, David Graham, and Baohua Gu

Terrestrial Ecosystem Science Program: NGEE-Arctic Project (PI: Stan Wullschleger)

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It has been estimated that almost half of the global soil organic carbon (SOC) is stored in Arctic permafrost ecosystems. During thaw, large quantities of greenhouse gases (GHG) such as CO<sub>2</sub> and CH<sub>4</sub> are released from biogeochemical transformations of SOC, which potentially provides a significant feedback to the global warming. To predict GHG production and to understand the pathways and mechanisms of SOC degradation in tundra soils, both field investigations at the Barrow Environmental Observatory (BEO) in Alaska and laboratory-scale incubation experiments were conducted. Field analyses of pore-water samples show both spatial and seasonal patterns of aqueous geochemistry in the active layer of low- and high-centered polygons. Dissolved Fe(II) and CH<sub>4</sub> in pore waters from saturated polygons increased with soil depth, and higher ratios of dissolved CH<sub>4</sub>/CO<sub>2</sub> were observed in late August than in early July. These observations corroborate with the results showing the decreased concentrations of small organic anions (e.g., acetate, formate, propionate, and butyrate) from July to August, suggesting that methanogenesis proceeded along with Fe(III) reduction from Spring to late Summer. Laboratory microcosm incubations were performed at ecologically relevant temperatures of -2 and 8 °C, and a suite of geochemical parameters including organic acids, carbohydrates, alcohols, Fe(II)/(III), and CH<sub>4</sub> and CO<sub>2</sub> were determined to assess the rates and pathways of Arctic SOC degradation under anoxic conditions. Microcosms at 8 °C showed a higher accumulation of organic acids than those at -2 °C in the organic layer, and greater consumption of organic acids was detected in the mineral layer than in the organic layer. We also found that common sugars (e.g., glucose, cellulose, xylose) degraded rapidly in the organic horizon, consistent with the high CO<sub>2</sub> production at early stage of the incubation. The biogeochemical processes we document here for anoxic tundra soils are thus pertinent to understanding organic matter decomposition as thaw depth and duration increase in permafrost, and the rates and pathways we identify will form the basis for a computational modeling framework in predicting feedbacks to warming climate.

## **Biogeochemical Controls on Microbial CO<sub>2</sub> and CH<sub>4</sub> Production in Polygonal Soils From the Barrow Environmental Observatory**

Terrestrial Ecosystem Science Program: NGEE-Arctic Project (PI: Wullschleger)

David E. Graham<sup>1</sup>, Taniya Roy Chowdhury<sup>1,4</sup>, Elizabeth M. Herndon<sup>2,5</sup>, Ziming Yang<sup>2</sup>, Liyuan Liang<sup>2</sup>, Baohua Gu<sup>2</sup>, and Stan D. Wullschleger<sup>2,3</sup>

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Organic matter buried in Arctic soils and permafrost will become accessible to increased microbial degradation as the ground warms due to climate change. The rates of organic matter degradation and the proportion of CH<sub>4</sub> and CO<sub>2</sub> greenhouse gasses depend on the microbial response to warming, organic carbon structure and availability, the pore-water quantity and geochemistry, and available electron acceptors. To adapt and improve the representation of these Arctic subsurface processes in terrestrial ecosystem models for the NGEE Arctic project, we examined SOM transformations from elevated and subsided areas of low- and high-centered polygons from interstitial tundra on the Barrow Environmental Observatory (Barrow, AK). Significant amounts of iron(II) ions in most organic and mineral soil horizons features indicate that newly thawed organic matter will be released into anoxic conditions. Using microcosm incubations at fixed temperatures and controlled thawing systems for frozen soil cores, we investigated the microbiological processes and rates of SOM degradation and greenhouse gas production under anoxic conditions, at ecologically relevant temperatures of -2, +4 or +8 °C. Incubated soils from low-centered polygons produced substantially more CH<sub>4</sub> and CO<sub>2</sub> than soils from corresponding positions of high-centered polygons regardless of water saturation, indicating additional controls on SOM degradation. Substantial differences in CH<sub>4</sub> and CO<sub>2</sub> response curves from different microtopographic samples separate the thermodynamic controls on biological activity from the kinetic controls of microbial growth and migration following thaw that together determine the temperature response for greenhouse gas emissions in a warming Arctic.

## ESS abstract

### Geochemical constraints on water, carbon, and nitrogen cycling at different scales in the tundra environment of Barrow, Alaska

Arctic tundra contains large carbon stocks stored in active layer soils and permafrost, and may be an important source of carbon dioxide and methane over the next century due to a rapidly changing climate, degrading permafrost, and redistribution of water across high latitude landscapes. The DOE Office of Science Biological and Environmental Research Program has funded the Next Generation Ecosystem Experiment (NGEE) Arctic project to quantify biogeochemical and biogeophysical processes and to develop model representations of terrestrial climate feedbacks from these systems. This presentation synthesizes geochemical and isotopic data and examines vertical and lateral factors and processes critical to predicting the carbon, nitrogen, and water balance of tundra ecosystems. Stable water isotope analyses ( $\delta D$  and  $\delta^{18}O$ ) indicate recharge of higher elevation microtopography and shallow saturated pore waters during summer thaw season from recent precipitation events, with stronger winter and seasonal ice melt contribution to deep pore waters in saturated troughs, ponds, and low-centered polygons. Microtopography and water table effects on geochemistry were also apparent from a comprehensive spatial examination of active layer biogeochemistry, showing a number of significant differences in the concentrations of cations and anions for polygonal type (i.e., high- versus low-centered ice wedge polygons), microtopographic features (polygonal centers versus troughs), and with depth. These results have implications for future nutrient availability. For example, permafrost degradation has the potential to produce a shift from low- to high-centered polygons. Our results showed higher concentrations of oxyanions (sulfate, phosphate, and nitrate) in high centered polygons versus low-centered polygons, suggesting potentially greater availability of these limiting nutrients with projected future microtopographic evolution. Nitrate isotopes ( $\delta^{15}N$  and  $\delta^{18}O$ ) indicated a predominantly microbial source for nitrate in high centered polygon active layers. However, there appears to be a greater component of atmospheric nitrate in permafrost that may serve as a potential indicator of permafrost degradation. Additionally, our results suggest that older, deeper carbon sources may be promoting a shift in methanogenic pathway, from predominantly acetoclastic to hydrogenotrophic. This mechanistic shift is attributed to the source and quality of available organic substrate. Overall, results showed substantial lateral and vertical variability in biogeochemical, biogeophysical, and hydrological processes across microtopographic- to landscape scales that needs to be accounted for in fine and intermediate scale models.

# **Application of Fully Coupled Hydrology and Biogeochemistry CLM-PFLOTRAN Model to Simulate Soil C Stocks at NGEE Arctic Intensive Study Sites at Barrow, Alaska**

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## **Abstract**

In nature soil biophysical and biogeochemical processes are coupled spatially and temporally, which could not be ignored in High-Resolution Land Surface Models (LSM), due to complexity of process interactions occurring in locally inter-connected systems. In the Community Land Model (CLM), the land component of the Community Earth System Model (CESM), soil C-N processes and thermal-hydrology are not only implemented sequentially but also lateral connections in subsurface are not considered. PFLOTRAN is an open source, state-of-the-art massively parallel 3-D subsurface flow and reactive transport code. In this study, we extend the subsurface hydrological process coupling between CLM and PFLOTRAN to explicitly include soil biogeochemical reactive transports. The resulting coupled CLM-PFLOTRAN model is a high-resolution LSM capable of resolving 3-D soil hydrological-thermal-biogeochemical processes.

The classic CLM-CN reaction networks, degassing-dissolving of C-N relevant greenhouse gas species among soil solution and air, and soil N absorption processes are implemented in PFLOTRAN's reactive-transport framework. We compare soil C stock estimates from CLM alone and coupled CLM-PFLOTRAN simulations at the Next Generation Ecosystem Experiment-Arctic sites at the Barrow Environmental Observatory (BEO), AK. These intensive study sites are featuring with polygonal micro-topographic units, such as trough, center/edge for low/high/flat-centered polygons, and non-polygonal ground. Simulated results are compared against available soil C dataset to assess importance of coupled reactive-transport processes at fine scale in LSMs. Contributions of both soils and plant function types (PFT) to spatial variance of soil C from the two modeling approaches are discussed. Results indicate that two modeling approaches could produce very contrasting results across micro-topographic units. The developed CLM-PFLOTRAN framework will be used for regional evaluation of climate change caused ecosystem process responses and their feedbacks to climate system.

Key word: Soil C stocks, soil biogeochemistry, soil thermal-hydrology, synchronization, sequential, CLM-CN model, PFLOTRAN model, polygonal coastal tundra

## **Mechanistic treatment of plant N use, root-microbe competition, and microbial processes improves high-latitude and global ecosystem carbon budget predictions**

W.J. Riley, N.J. Bouskill, B. Ghimire, C.D. Koven, J. Tang

The current versions of the Community Land Model perform poorly when compared to carbon, hydrological, and energy budget observations in high latitude systems. Among the several modeling goals for NGEE-Arctic is the improvement of these processes in CLM so that realistic predictions of the C-climate feedbacks can be integrated in an Earth System Model (CESM or ACME). We report here on modeling progress in CLM that the Berkeley Lab group has recently made to improve representation of (1) nutrient controls on photosynthesis; (2) competition between roots and microbes for nutrients; (3) a microbial model of nitrogen fixation; and (4) interactions between microbes, enzymes, and mineral surfaces. We also present a meta-analysis approach using results from dozens of high-latitude temperature and nutrient addition experiments to evaluate CLM responses to these perturbations. We show that the current method of representing nutrient controls on photosynthesis results in unrealistic nitrogen perturbation responses and diurnal cycles of GPP. Our approach that prognoses leaf nitrogen and its impact on photosynthesis and more realistically represents the below- and above-ground competitive environment dramatically improves site-level and global-scale comparisons with observationally derived metrics.

## Improving the representation of Arctic photosynthesis in Earth System Models

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The primary goal of Earth System Models (ESMs) is to improve understanding and projection of future global change. In order to do this models must accurately represent the terrestrial carbon cycle. Although Arctic carbon fluxes are small relative to global carbon fluxes, uncertainty is large. Photosynthetic CO<sub>2</sub> uptake is well described by the Farquhar, von Caemmerer and Berry (FvCB) model of photosynthesis and most ESMs use a derivation of the FvCB model to calculate gross primary productivity. Two key parameters required by the FvCB model are an estimate of the maximum rate of carboxylation by the enzyme Rubisco ( $V_{c,max}$ ) and the maximum rate of electron transport ( $J_{max}$ ). In ESMs the parameter  $V_{c,max}$  is typically fixed for a given plant functional type (PFT). Only four ESMs currently have an explicit Arctic PFT and the data used to derive  $V_{c,max}$  in these models relies on small data sets and unjustified assumptions. We examined the derivation of  $V_{c,max}$  and  $J_{max}$  in current Arctic PFTs and estimated  $V_{c,max}$  and  $J_{max}$  for a range of Arctic PFTs growing on the Barrow Environmental Observatory, Barrow, AK. We found that the values of  $V_{c,max}$  currently used to represent Arctic plants in ESMs are 70% lower than the values we measured, and contemporary temperature response functions for  $V_{c,max}$  also appear to underestimate  $V_{c,max}$  at low temperature. ESMs typically use a single multiplier ( $JV_{ratio}$ ) to convert  $V_{c,max}$  to  $J_{max}$ , however we found that the  $JV_{ratio}$  of Arctic plants is higher than current estimates suggesting that Arctic PFTs will be more responsive to rising carbon dioxide than currently projected. In addition we are exploring remotely sensed methods to scale up key biochemical (e.g. leaf N, leaf mass area) and physiological (e.g.  $V_{c,max}$  and  $J_{max}$ ) properties that drive model representation of photosynthesis in the Arctic. Our data suggest that the Arctic tundra has a much greater capacity for CO<sub>2</sub> uptake, particularly at low temperature, and will be more CO<sub>2</sub> responsive than is currently represented in ESMs. As we build robust relationships between physiology and spectral signatures we hope to provide spatially and temporally resolved trait maps of key model parameters that can be ingested by new model frameworks, or used to validate emergent model properties.

## **Scaling plant physiology for Earth System Models (ESMs)**

Shawn Serbin (Brookhaven National Laboratory)

Alistair Rogers (Brookhaven National Laboratory)

Richard Norby (Oak Ridge National Laboratory)

Jin Wu (University of Arizona)

Scott Saleska (University of Arizona)

### **Abstract**

Ecosystem and Earth System Models (EESMs) require detailed information on ecosystem states and canopy properties in order to properly represent the carbon (C) cycle and simulate the fluxes of C, water and energy from the land to the atmosphere as well as address the vulnerability of ecosystems to environmental and other perturbations. Moreover, EESM uncertainty is currently dominated by model parameter uncertainty stemming from inadequate representation of plant traits. Over the last several decades the amount of available data to constrain ecological predictions has increased substantially, resulting in an increasingly data-rich era for global change research. Remote sensing approaches, particularly spectroscopy, imaging spectroscopy (IS) and thermal infrared (TIR) data, represent a synoptic observational dataset capable of capturing broad-scale spatial and temporal dynamics in many important vegetation properties related to terrestrial ecosystem functioning, offering an important and direct data constraint on ecosystem model projections.

Here we highlight ongoing work as part of the Next Generation Ecosystem Experiment (NGEE) Arctic (NGEE-Arctic) and developing Tropics (NGEE-Tropics) projects, as well as the ongoing NASA HypIRI Airborne Campaign (<http://hyspiri.jpl.nasa.gov/airborne>), to develop a generalized framework for scaling and mapping plant physiological traits with remote sensing approaches including the quantification of uncertainties in trait estimates. Specifically, we are focusing on key vegetation properties related to C uptake, water and energy fluxes,

as well as nutrient cycling, including biochemical (e.g. leaf N, ligno-cellulose), morphological (e.g. leaf mass area, LMA), and physiological (e.g.  $V_{c,max}$  and  $J_{max}$ ) traits that drive model representation of gross and net primary productivity. For example, preliminary results, at the leaf level, indicate a strong capacity to generalize the relationship between spectral optical properties and LMA across global biomes from the Arctic to the Tropics. In general our results, across a range of scales, highlight the potential to develop general algorithms for a number of key traits needed for EESM model parameterization or initialization, as well as for capturing broad-scale responses of ecosystems to environmental perturbations. This approach provides the data products necessary to enable a transformational change in representation of plant traits in next generation EESMs.

**Multi-scale evidence of CO<sub>2</sub> and CH<sub>4</sub> emissions during spring thaw  
from Northern Alaska**

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Understanding Arctic carbon emissions is critical for predicting climate change feedbacks and closing the global carbon budget. The few observations of tundra greenhouse gas (GHG) fluxes before snowmelt suggest there may be large pulses of CO<sub>2</sub> and CH<sub>4</sub> during spring thaw, but little is known about underlying mechanisms, and whether they influence regional atmospheric concentrations. To address these issues, we combined ecosystem-scale observations of GHG fluxes, a mechanistic soil-core thawing experiment, and airborne observations of atmospheric GHG concentrations. We show that during the 2-week period of snow and surface-ice melt, there were pulses of GHGs that contributed 6% of the snow-free season CH<sub>4</sub> emissions and not only offset 29% of total growing-season CO<sub>2</sub> uptake, but made the snow-free season from near carbon-neutral to a net source of atmospheric CO<sub>2</sub>. The controlled thaw released an immediate, large pulse of GHGs that had been trapped

under the surface ice, suggesting that biogenic production in autumn contributes to the spring pulse events. Regional atmospheric GHG mixing ratios, measured by aircraft, were elevated and had similar CO<sub>2</sub>/CH<sub>4</sub> ratio as the in situ and core pulses. Thus, this phenomenon is widespread enough to influence the regional atmospheric budget, and although Arctic tundra is widely classified as a carbon sink, our results show that taking into account snow-season GHG pulses reveals these Arctic tundra locations to be a net source of CO<sub>2</sub> to the atmosphere.

**Next Generation  
Ecosystem  
Experiments  
(NGEE) Tropics  
Abstracts**

## **Next Generation Ecosystem Experiments (NGEE) Tropics: Overview**

Tropical forests cycle more carbon and water than any other biome, and play critical roles in determining the Earth's energy balance. Yet there are large uncertainties regarding tropical forest response to a changing atmosphere and a warming climate. Many of these uncertainties are linked to how tropical forests interact with the global carbon cycle. First, intact tropical forests have been identified as a major sink for carbon, presumably driven by enhanced productivity under the rising concentration of atmospheric CO<sub>2</sub>. Second, deforestation and degradation of tropical forests result in large CO<sub>2</sub> emissions. Third, regrowth of secondary forests on anthropogenic landscapes is estimated to be an additional large carbon sink. These major shifts in tropical forest carbon cycling also have important impacts on water and energy fluxes. To develop robust projections of these responses over the next century, the current treatment of tropical forests in Earth system models (ESMs) must be improved, requiring a major research effort to codify our best process based knowledge of tropical forest functioning. This effort will include both a rigorous knowledge assessment using the available data, and new field investigations that target improved representations of critical processes. This poster will overview our NGEE Tropics modeling and data frameworks to address these challenges, and associated field activities in three process areas: (1) forest carbon cycle hydrology interactions, (2) disturbance and recovery processes (both natural and anthropogenic), and (3) pantropical variability in nutrient constraints on productivity.

## Improving understanding and modeling of hydrology-carbon interactions in NGEE-Tropics

L. Ruby Leung and the NGEE-Tropics Team

The U. S. Department of Energy is initiating a Next Generation Ecosystem Experiment (NGEE) in the tropics with the overarching goal of improving the ability of Earth System Models for predicting whether tropical forests will act as net carbon sinks through the 21<sup>st</sup> Century. As climate models projected increasing frequency and intensity of drought in the future, a key question that will be addressed is how tropical forests respond to drought. Through changes in water availability, drought can influence stomatal conductance that affects transpiration and carbon assimilation and allocation. Understanding and modeling hydrology-carbon interactions are thus critical to determining tropical forest response to drought and the impacts on the carbon cycle. This presents significant challenges for earth system modeling as the processes involved span a wide range of temporal and spatial scales, and plant response depends on hydraulic traits that may vary substantially across the diverse species of the tropical forest. Previous studies using data from drought experiments showed that models have limited skill in predicting drought response, but introducing mechanistic processes such as plant hydraulics into physiological-based models can improve prediction of drought-induced mortality. There are large uncertainties in modeling carbon assimilation due to uncertain parameters partly related to the use of fitted gas exchange data, and uncertain model structures because of different assumptions about canopy physiological processes. Similarly, hydrology models with different process representations and abilities to capture spatial heterogeneity may simulate very different soil moisture and groundwater accessible by plants under droughts. This poster will discuss a set of initial research activities in NGEE Tropics to quantify uncertainty and address gaps in modeling hydrology and carbon processes. A pilot study in the Amazon will provide an integrative test-bed for hydrology-carbon interactions. Building on the existing infrastructures at Manaus, the pilot study will contribute additional co-located hydrology and carbon measurements. Combined with the development of synthesized datasets, quantifying model uncertainty, and evaluating different modeling approaches, we aim to make important progress towards modeling of tropical forest response to drought in a pan-tropical context.

## Soil Biogeochemistry and Nutrient Constraints on Productivity within the NGEE-Tropics Research Program

Richard J. Norby and the NGEE-Tropics Team

The U. S. Department of Energy is initiating a Next Generation Ecosystem Experiment (NGEE) in the tropics with the overarching goal of determining if tropical forests will act as net carbon sinks through the 21<sup>st</sup> Century. Throughout the expected 10-year research program, we will be developing through a close integration of modeling and measurement a representative, process-rich tropical forest ecosystem model in which the evolution and feedbacks of tropical ecosystems in a changing climate can be modeled at the scale and resolution of a next generation Earth System model grid cell. A critical component of this exercise will be to include model structures and processes that help to address the question: “How will the response of tropical forests to climate change be modulated by spatial and temporal heterogeneity in belowground processes?” Belowground processes that control nutrient availability provide a primary control on the tropical carbon sink. We know that tropical forest productivity varies across fertility gradients, but this is poorly represented in current models, which lack processes of nutrient availability, uptake, and physiological responses to nutrient limitation. Especially important for modeling tropical ecosystems will be including a phosphorus cycle and a physiologically-based representation of phosphorus limitation of productivity. To address this need, we will take an integrative approach, starting with insights from models and model uncertainty and guided by the need to inform and improve nutrient interactions in models. An initial focus will be on improving the phosphorus model through targeted measurements in a field campaign in Puerto Rico. The objective will be to make model-guided measurements to link soil chemistry, rhizosphere microbial activity, and root traits with P availability and uptake. Working across orthogonal transects of varying soil phosphorus availability and a range of forest development, we will employ a systems biology approach to microbial and plant function related to phosphorus availability, phosphorus acquisition, and nitrogen-phosphorus interactions. Belowground traits will be linked with more easily observable aboveground traits, including foliar nitrogen and phosphorus concentrations and spectral signatures that will inform spatial scaling. Disturbance patterns and secondary forest development have a large influence on the tropical carbon sink and alter the relationship between soil fertility and forest productivity, for example by shifting nutrient limitation from phosphorus to nitrogen. We will link the mechanistic studies of phosphorus availability to a broader scale quantification of forest biomass and leaf traits across a successional gradient using a multi-sensor, airborne, remote-sensing platform.

# **University Abstracts: SBR Oriented**

## Mercury stable isotope exchange between dissolved Hg(0) and Hg(II)-thiol complexes

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**Background:** Mercury (Hg) stable isotopes have been employed to trace Hg sources and chemical transformations in the environment. In anoxic waters, dissolved Hg(0) and Hg(II)-complexes often coexist but the isotope exchange between mercury species is poorly understood. In this study, we carried out laboratory experiments to examine Hg stable isotope exchange between dissolved Hg(0)-Hg(II)-thiol complexes.

**Research Methods:** Experiments were performed to determine the rate at which isotopes are exchanged and isotopic equilibrium between dissolved Hg(0) and thiol-complexed Hg(II) under anoxic conditions. The dissolved Hg(0) pool was generated by a metallic Hg bead in a silicone tube, equilibrated with water. The Hg(0) in solution was then partially oxidized to form Hg(II). The Hg(0)/Hg(II) solution was reacted with either mercaptoacetic acid (MCA), mercaptopropionic acid (2-MPA), cysteine, or humic acids. The aqueous Hg(II) was allowed to complex with the thiol ligand. Once chemical equilibrium was reached, reactors were periodically sacrificed for isotopic analysis. For mass spectrometry, samples were diluted, then spiked with a calibrated <sup>204</sup>Hg/<sup>196</sup>Hg double spike. Isotopic compositions (<sup>199</sup>Hg/<sup>198</sup>Hg, <sup>200</sup>Hg/<sup>198</sup>Hg, <sup>201</sup>Hg/<sup>198</sup>Hg, <sup>202</sup>Hg/<sup>198</sup>Hg) were measured on a Nu Plasma multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS).

**Results:** At the beginning of the experiment, the Hg(0)/Hg(II) solution showed a  $\delta^{202}\text{Hg}$  difference between the Hg(II) pool and the dissolved Hg(0) pool of 2.4‰. Addition of MCA caused Hg(II) to complex with thiol groups, and initially the Hg(II) retained its isotopic composition. Isotopic exchange between the Hg(II)-thiol complexes and the Hg(0) occurred within the first 12 hours, driving both toward isotopic equilibrium. After 48 hours, the equilibrium isotopic fractionation between Hg(0) and thiol-Hg(II) was approximately 0.7 ‰. The results suggest that Hg isotope ratios can be affected without chemical transformations taking place. In our presentation, we will discuss the implications of our findings for interpreting isotopic data collected for groundwater containing both Hg(0) and Hg(II) species.

## Fate of Uranium in Wetlands: Impact of Drought followed by Re-flooding

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Uranium contamination in groundwater can be mitigated in anoxic zones by iron-reducing bacteria that reduce soluble U(VI) to insoluble U(IV) and by uranium immobilization through complexation and sorption. Wetlands often link ground and surface-waters, making them strategic systems for potentially limiting migration of uranium contamination of water resources. Little is known about how drought periods that result in the drying of wetland soils, and consequent redox changes, affect uranium fate and transport in wetlands. In order to better understand the fate and stability of immobilized uranium in wetland soils, and how dry periods affect the uranium stability, we dosed saturated wetland mesocosms planted with *Scirpus acutus* with low levels of uranyl-acetate for 5 months before imposing a 9-day drying period followed by a 13-day rewetting period. Concentrations of uranium in mesocosm effluent increased after rewetting, but the cumulative amount of uranium released in the 13 days following the drying constituted less than 1% of the uranium immobilized in the soil during the 5 months prior to the drought. This low level of remobilization suggests that the uranium immobilized in these soils was not primarily bioreduced U(IV), which could have been oxidized to soluble U(VI) during the drought and released in the effluent during the subsequent flood. XANES analyses confirm that most of the uranium immobilized in the mesocosms was U(VI). Compared to mesocosms that did not experience drying or rewetting, mesocosms that were sacrificed immediately after drying and after 13 days of rewetting had less uranium in soil near roots and more uranium on root surfaces. Mapping of uranium and iron on root samples before and after drying has been performed to understand whether this migration of uranium is attributable to coprecipitation or sorption of dislodged uranium on roots' iron oxide coatings. Results show that short periods of drought conditions in a wetland may impact uranium distribution, but these conditions may not cause large losses of immobilized uranium from the wetland. Further experiments investigated the possibility of links between uranium immobilization and nitrogen cycling in wetlands. A recently identified *Acidimicrobiaceae* bacterium (A6) derives energy from ammonium oxidation coupled with iron reduction. This bacterium has been found in uranium-contaminated wetland sediments at the Savannah River Site. Lab experiments have demonstrated that A6 can use U(VI) as an electron acceptor in the presence of ammonium, suggesting that natural sites of active ammonium oxidation by A6 could be hotspots of uranium immobilization.

Seeing What a Microbe Sees: Real-Time Geochemical Monitoring with 'Geo-Sense'  
Toshiyuki Ueki, Dawn E. Holmes, David Walker, Kelly P. Nevin, and Derek R. Lovley

A limitation in biogeochemical modeling is a lack of real-time data on the *in situ* geochemical environment that directly impacts on microbial activity. Traditional analytical methods are often unable to distinguish speciation and/or complexation of molecules that have important influences on the interaction of those molecules with microbial enzymes. Furthermore, invasive sampling techniques, as well as the associated labor and analytical costs, prevent real-time analyses and limit the extent to which environmental heterogeneities and perturbations can be explored. We previously described SMART (Subsurface Microbial Activity in Real Time) technology, which provides real-time, continuous estimates of the overall rates of microbial activity in anaerobic soils and sediments. SMART takes advantage of the fact that the current-producing activity of microbes that colonize electrodes inserted into anaerobic soils reflects the activity of microbes in the nearby surrounding soil. In order to better understand the factors that control these rates of microbial activity, we are developing 'Geo-Sense' real-time biological sensors. Geo-Sense biosensors are designed to continuously report on the concentrations of important geochemical constituents that bacteria actually sense. The biosensors are constructed with strains of *Geobacter sulfurreducens* that specifically produce an electrical current in response to chemicals that interact with engineered genetic regulatory circuits. In this manner, the electrical response is to the biologically available fraction of nutrients or inhibitory compounds, providing a more microbiologically relevant analysis compared with bulk chemical analysis. Although biological sensors based on current-producing microorganisms have been described previously, those sensors relied on controlling the expression of proteins necessary for electron transfer to electrodes. This approach yields slow response times and lacks resolution. Geo-Sense biosensors utilize a different approach to control the current output. Proof-of-concept studies with either isopropyl  $\beta$ -D-1-thiogalactopyranoside (IPTG) or anhydrotetracycline as the inducer yielded promising results and Geo-Sense strains have now been produced for the detection of iron, arsenic, or mercury. The Geo-Sense platform offers the potential for construction of a wide diversity of chemicals for which a microbial sensor system can be identified. To date Geo-Sense has only been tested in controlled laboratory conditions. However, a strategy for field deployment based on our previously patented microbial fuel cell technology has been developed. It is expected that coupling Geo-Sense and SMART technologies will make it feasible to inexpensively and remotely collect real-time data not only on rates of microbial activity but important geochemical parameters influencing microbial activity in a diversity of soils and sediments.

## Electron Transfer and Atom Exchange Between Fe(II) and Structural Fe(III) in Clays

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Clay minerals are ubiquitous in soils, sediments, and aquatic environments, and contain a significant proportion of the iron present in these environments. Fe-bearing clay minerals serve as an important source and sink for electrons in redox reactions in various subsurface geochemical environments. The 2:1 tetrahedral-to-octahedral smectite clay minerals contain a wide range of Fe contents from trace (e.g. montmorillonites) to 30% of their mass (e.g. nontronites). Here we focus on the redox reaction between aqueous  $\text{Fe(II)}_{\text{aq}}$  and structural  $\text{Fe(III)}_{\text{clay}}$  in smectites. We isolate the reduction of  $\text{Fe(III)}_{\text{clay}}$  by  $\text{Fe(II)}_{\text{aq}}$  using the isotope specificity of  $^{57}\text{Fe}$ -Mössbauer spectroscopy. In experiments with Mössbauer-inactive  $^{56}\text{Fe(II)}$ , we observe more relative reduction of  $\text{Fe(III)}_{\text{clay}}$  by  $\text{Fe(II)}_{\text{aq}}$  for the low-Fe clay mineral SWy-2 (67% reduction) than for high-Fe containing nontronites NAu-1 and NAu-2 (10-20% reduction). Mössbauer spectra suggest that electrons are localized in SWy-2 as distinct  $\text{Fe(II)}_{\text{clay}}$  species, which contrasts with the observed hopping of electrons between  $\text{Fe(II)}_{\text{clay}}$  and  $\text{Fe(III)}_{\text{clay}}$  for the nontronites. Our observations are consistent with clustering of Fe atoms in the nontronites but not SWy-2.

We also use enriched isotope tracers to track movement of Fe atoms between solution and the structure of the clay minerals. Our results indicate up to nearly 20% exchange between  $\text{Fe(II)}_{\text{aq}}$  and NAu-2 over 6 months in pH 7.5 suspension, with less, but still significant amounts of exchange at pH 6.0. The clay minerals SWy-2 and NAu-1 exchange approximately 7 to 10% of their Fe with solution. Our calculations indicate that these levels of exchange require mixing of at least 2-3 unit cells deep, and suggest that a significant amount of Fe in the clay mineral structure is susceptible to reduction and atom exchange.

## **Radiocarbon Signature of Microbial DNA and RNA from a Reducing Zone of a Floodplain aquifer, Rifle Colorado**

*University-Led Research, SBR*

Brian J. Mailloux (PI) - Barnard College;

Alison Spodek Keimowitz - Vassar College;

James F Ranville, Valerie Stucker, Jonathan O. Sharp - Colorado School of Mines;

Kenneth H. Williams – LBNL

Bruce Buchholz - LLNL

Biogeochemical redox cycles in groundwater systems frequently mobilize metals and metalloids that directly impact human health. The microbes catalyzing these biogeochemical reactions require organic carbon as an electron donor. The source(s) of these electron donors in groundwater systems has been at best poorly constrained. We recently developed a method to filter large volumes of groundwater (>2000 gallons), extract and purify the DNA, and to radiocarbon date the DNA to determine organic carbon sources (Mailloux et al., 2013). Results from one high arsenic field site in Bangladesh characterized by rapid infiltration indicated that microbes preferentially used organic carbon that was slowly advected through the aquifer. Microbes did not utilize young anthropogenic organic carbon nor did they utilize sediment derived organic carbon. At the Department of Energy's Field Research Challenge (IFRC) site near Rifle, Colorado portions of the recently recharged shallow aquifer are reducing with elevated levels of arsenic and iron. In addition, this aquifer harbors novel microbial assemblages. This aquifer offers a unique opportunity to study organic carbon sources given the different potential and resolvable organic carbon sources. The organic carbon sources include modern organic carbon from recent recharge, slowly advected organic carbon represented by dissolved organic matter (DOM), and older sediment organic carbon. Estimated groundwater flow rates are 80 m per year indicating that the sight is flushed approximately annually. Two samples of DOM from the site were dated at 2980 and 3340 y. Bulk radiocarbon sediment ages ranged from 4750 to 11,600 y. Well LQ-107 with 2.2 mg/l Fe and 62 ug/l arsenic was sampled to determine organic carbon sources. Water was filtered using a 10" filter housing and 0.2  $\mu\text{m}$  serial nylon filters. The planktonic microbial population was sampled by filtering 6213 gallons. DNA was extracted and purified to remove organic carbon derived from the cell lysates, humic materials, and buffers. DNA was radiocarbon dated at the Center for AMS at Lawrence Livermore National Laboratory. The Radiocarbon DNA age was 3325 $\pm$ 40 y. In addition we are currently awaiting RNA radiocarbon dates. These results indicate that the microbial population at the site is utilizing the DOM for cell division. Future plans include sampling more wells and completing development of an RNA radiocarbon method.

Mailloux, B.J., Trembath-Reichert, E., Cheung, J., Watson, M., Stute, M., Freyer, G.A., Ferguson, A.S., Ahmed, K.M., Alam, M.J., Buchholz, B.A., Thomas, J., Layton, A.C., Zheng, Y., Bostick, B.C., van Geen, A., 2013. Advection of surface-derived organic carbon fuels microbial reduction in Bangladesh groundwater. PNAS 110, 5331-5335.

## Competitive Complexation of Mercury with Thiols from Natural Organic Matter and Bacterial Cell Envelopes

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Thiols are known to control the speciation and bioavailability of Hg by 1) providing high-affinity binding sites, 2) mediating redox transformations, and 3) controlling precipitation and colloidal formation. Natural organic matter (NOM) is considered the main sources of thiols in aquatic environments, and is believed to control the fate of Hg. Our studies have shown that bacterial cell envelopes are an additional source of thiols in aquatic and terrestrial systems. Complexation of Hg with thiols associated with NOM is similar to that of cell envelopes in many regards. The discovery of Hg-thiol binding on bacterial cell envelopes raises the question of the relative importance of NOM compared to cells in controlling the overall fate and transport of Hg. Using Suwanee River Fulvic acid (FA) as a proxy for NOM, we conducted Hg and S X-ray Absorption Spectroscopy (XAS) experiments to evaluate the chemical reactivity and stability of Hg complexed with NOM and bacterial cell envelopes.

Hg XANES and EXAFS spectroscopic results indicate that Hg binds predominantly to the high-affinity thiol groups on bacterial cell envelopes in the presence and absence of FA. Hg binding mechanisms with the bacterial biomass do not change in the presence of FA, ruling out the possibility of the formation of ternary complexes. Additionally, pH does not affect the binding mechanism of Hg onto biomass in the presence of FA. Hg XAS results suggest that thiols on *Shewanella oneidensis* MR-1 cell envelopes out-compete thiols in FA for Hg binding, and similarly S XANES results suggest that, on an average Hg binding to FA appears weaker than Hg binding to bacterial biomass. S XANES measurements of *S. oneidensis* MR-1 show that nearly the entire S budget of the biomass is present as reduced S groups, a fraction of which is known to form strong bonds with Hg. However, FA has a range of reduced and oxidized S species.

In summary, the speciation and distribution of Hg bound to NOM or bacteria is highly sensitive to their relative concentrations and to the specific make-up of thiol within each complexant. We have conducted further studies to understand the nature and behavior of Hg complexation with several NOM and DOM of varying age and composition. Our studies illustrate weakening of the binding strength of Hg complexation with DOM as a function of age, probably due to slow oxidation of thiols in DOM. Clearly, further studies are required to understand the reactivity and stability of Hg bound to NOM and bacterial thiol sites.

## ***Anaeromyxobacter dehalogenans* Strain 2CP-C Employs Distinct Metabolic Activities for Growth with Metal vs. Non-metal Electron Acceptors**

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*Anaeromyxobacter dehalogenans* strain 2CP-C is a facultative Gram-negative Gamma-proteobacterium related to the *Myxobacteria*. Unlike other members of *Myxobacteria*, which were considered obligate aerobes, *A. dehalogenans* is capable of growth and survival in anoxic and suboxic environments. Studies of anaerobic growth of strain 2CP-C revealed tremendous respiratory versatility, as evidenced by the ability to utilize a range of electron donors (e.g. acetate, hydrogen, pyruvate, lactate, succinate, formate) and electron acceptors (e.g. nitrate, fumarate, halogenated phenols, ferric iron, nitrous oxide, etc.). In particular, the dissimilatory metabolic reduction of metals, including radionuclides, by strain 2CP-C spurred interest for *in situ* bioremediation of contaminated soils and sediments.

In order to understand the cellular mechanisms that enable this microbe to survive under different environmental conditions, a mass spectrometry-based proteomics approach was implemented to characterize the proteome profiles of strain 2CP-C grown with various electron acceptors. A total of eight growth conditions were tested, providing a global survey of the proteome-wide responses to different electron acceptors. The pan-proteome consists of 2,846 proteins, representing 65% of predicted open reading frames. The results also revealed a core proteome of 710 proteins that comprise the fundamental cellular machinery needed regardless of varying electron-accepting environments. To visualize proteins significantly changed between growth conditions, differentially abundant proteins were mapped to metabolic pathways in KEGG database using iPath 2.0. Significantly abundant proteins in metal electron acceptor growth mapped to metabolic pathways participating in the TCA cycle, and amino acid, nucleotide and carbohydrate metabolism, whereas significantly abundant proteins in non-metal electron acceptor growth mostly involved in regulatory pathways for translation and cell motility. Metabolic pathways mapping clearly indicated elevated expression of energy production pathways in growth with metal electron acceptors. Amino acid and nucleotide metabolism also demonstrated significant higher abundance levels in metal electron acceptor- growth, which could be a result of overall higher expression of energy-generating pathways in cells grown with metal electron acceptors.

Taken together, the ANOVA analysis and pathway mapping results demonstrated the distinct effects of metal and non-metal growth conditions on the proteome expression of *A. dehalogenans* strain 2CP-C. In particular, growth with metal electron acceptor resulted in elevated abundances for proteins involved in energy production compared to cells using non-metal electron acceptors.

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## **Radionuclide Waste Disposal: Development of Multi-scale Experimental and Modeling Capabilities** *University-Led Research*

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This project is a Department of Energy, Experimental Program to Stimulate Competitive Research (EPSCoR) Implementation Grant. The experimental and modeling efforts of this project are guided by the overarching scientific question:

*What are the major molecular level chemical, biological, and microbial interactions that control the mobility of radionuclides in natural and engineered systems and how can these molecular and pore scale processes be properly defined and quantified for incorporation into larger scale, coupled experimental systems and reactive transport modeling efforts?*

The key issues to be addressed include identifying source terms for contaminants in geologic disposal scenarios, determining the chemical speciation of risk-driving radionuclides (*e.g.*, Np, Tc, Cs, U, I) within engineered waste forms and natural subsurface environments, delineating the biogeochemical and physical processes through which contaminant transport is manifested, and predicting contaminant mobility across wide temporal and spatial scales. The project is undertaken by an interdisciplinary team from three South Carolina universities. The project is divided into four major tasks as well as the development of a new imaging facility capable of monitoring the 2D and 3D transport of radionuclides through engineered waste forms and natural soils.

Major accomplishments of the project to date include:

- Testing of Single Photon Emission Computed Tomography (SPECT) imaging systems using a column with an idealized soil structure.
- Design and groundbreaking on a field lysimeter facility used to monitor transport of U, Tc, Np, I, and Cs under natural conditions.
- Experimental and quantum-mechanical modeling studies of hollandite compositions of the form  $Ba_xCs_{2.32-2x}Ga_{2.32}Ti_{5.68}O_{16}$  are underway with varying A site (Ba/Cs) composition.
- Characterization of Tc behavior in reducing grout/cementitious waste forms under controlled laboratory and field conditions have examined the rate of Tc(IV) oxidation to  $Tc_2S_7$  and  $TcO_4^-$ . Complimentary studies are underway to examine the use of graphitic nanoreinforcements to alter strength and porosity of the waste form.
- Component additivity surface complexation models describing Tc, U, and Cs sorption to a Savannah River Site sandy loam soil have been developed.
- A kinetic model describing competitive ion sorption processes has been developed which can account for competition between weakly and strongly sorbing ions across a wide range of concentrations. A kinetic rather than equilibrium model is needed to account for the expected disequilibrium within pore waters.

## **Development of a Self-Consistent Model of Plutonium Sorption: Quantification of Sorption Enthalpy and Ligand-Promoted Dissolution**

*University-Led Research*

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The overarching objective of this work is to develop a thermochemical model of Pu sorption to minerals and sediments that incorporates aqueous and solid phase speciation, redox reactions, and the influence of organic ligands. This has been done using a suite of techniques including variable temperature batch sorption, x-ray absorption spectroscopy, quantum mechanical modeling, and isothermal titration calorimetry.

This work has taken a detailed approach to understanding the reactivity of Pu and other actinides with goethite, hematite, and kaolinite surfaces and describe the data using a surface complexation modeling approach. The specific surface complexes in these models have been constrained to the extent possible by direct (x-ray absorption spectroscopy, XAS) and indirect (solvent extraction) methods of determining the Pu oxidation state and chemical species. For example, batch sorption and x-ray absorption near edge spectroscopy (XANES) starting with either Pu(III), Pu(IV), or Pu(V/VI) have demonstrated that Pu(IV) becomes the dominant oxidation state on quartz and hematite surfaces regardless of the initial oxidation state. Furthermore, variable temperature batch sorption experiments have demonstrated sorption of Eu(III), Th(IV), Pu(IV), Pu(V), and Np(V) to goethite (and hematite for Eu) increases with increasing pH and increasing temperature. The data indicate sorption is endothermic and that the increase in sorption with temperature is driven by a positive entropy. These measurements are consistent with the experimental hypothesis that removal of hydrating waters provides an entropically driven free energy of these sorption reactions. This behavior has been supported using XAS and quantum mechanical modeling.

The surface complexation models described above have been used to describe Pu sorption and redox reactions with soils from the Savannah River Site and the Hanford 200 Area using a component additivity approach which accounts for specific mineral phases within each soil. The models are capable of predicting the degree of sorption observed on relatively short time scales. However, observations of Pu desorption from a SRS soil which has been contaminated with Pu for 30+ years indicate that desorption is either drastically kinetically hindered or irreversible. Thus, there appears to be an aging effect that is not currently accounted for in our thermochemically based modeling approach. The results from these experimental measurements are being compared with quantum mechanical calculations of actinide interactions with pure mineral phases. Current experimental efforts are focused on characterizing changes in Pu(IV) and Pu(V) source materials used in a new set of field lysimeter experiments called the Radiological Field Lysimeter Experiment (RadFLEX) at the SRS.

# Plutonium Immobilization and Mobilization by Soil Organic Matter

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Pu is believed to be essentially immobile in groundwater due to its low solubility and high particle reactivity to mineral phase or natural organic matter (NOM). However, previous studies reported Pu can be transported several kilometers in surface water systems, in the form of a colloidal organic matter carrier, through wind/water interactions. The role of NOM in both immobilizing or re-mobilizing Pu thus has been demonstrated. For example, in sediments collected from SRS, close to a wetland and a groundwater plume, <sup>239,240</sup>Pu concentrations are more closely correlated with organic nitrogen content than the bulk organic carbon content, suggesting <sup>239,240</sup>Pu immobilization by nitrogen-containing organic compounds. More intriguingly, hydroxamate siderophores, which are a strong iron-complexing ligand produced by microbes, are shown to be one class of the nitrogen-containing compounds (0.15-5.51% of total organic nitrogen) and are thought to be responsible for scavenging and fixing Pu in the sediment, due to its high binding constants. Additional supporting evidence that nitrogen-containing organic compounds control Pu transport was obtained from surface soil cores from three distinct soil types: paddy soil, deciduous soil and coniferous soil in the Fukushima Prefecture after the FDNPP accident. Although Pu was believed to be mostly contributed by global fallout, atmospheric fallout from 1963-1979, and atomic bomb events prior to the FDNPP accident, we found that Pu was strongly associated with organic nitrogen in these sediments, too. Electrospray Ionization-Fourier Transform Ion Cyclotron Mass Spectrometry (ESI-FTICRMS) was applied to investigate the Pu enriched fraction, which was collected from a surface sediment soil of the SRS by several separation and purification steps: 1) soil leaching by artificial groundwater; 2) filtration and ultrafiltration to obtain the 0.45 μm to 1 kDa fraction; 3) isoelectric focusing electrophoresis (IEF) experiment to obtain the Pu-enriched fraction; 4) ultrafiltration to rinse off the detergent and buffer. Pu-enriched macromolecules mostly belong to the class of lipids, but are also contributed by lignin, proteins, unsaturated hydrocarbons and condensed hydrocarbons. Formulas of the nitrogen-containing compounds overlap with the bulk formulas. A comparison of the mass spectra of DFO-B and Pu-enriched macromolecules confirm the presence of siderophores in this Pu organic carrier phase. It is thus very likely that hydroxamate siderophores, with a molecule weight of less than 1 kDa, together with other unknown nitrogen-containing compounds, were once produced by microbes and then incorporated into a large macromolecule. This provides a novel mechanism for surface Pu migration in organic-rich terrestrial systems.

A comparison of Hg(II) uptake and accumulation between mercury methylating and non-methylating bacteria.

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Hg(II) uptake is a key first step in the methylation of Hg(II) by anaerobic bacteria and thus, conditions affecting its transport greatly influence the amount of methylmercury which accumulates. Experiments with mercury methylating and non-methylating bacteria support a common active Hg(II) uptake mechanism inhibited by Zn(II) and Cd(II) but not other divalent metals. Thus, Hg(II) uptake appears to be a result of accidental import during the acquisition of essential trace metals, such as Zn(II). While the mechanism and rate of uptake is remarkably similar in methylating and non-methylating bacteria, differences have been observed in Hg bioavailability to organisms living at different redox zones. For instance, a fermentative firmicute, *Ethanoligenes harbiense*, had low affinity for Hg(II) and exhibited the lowest accumulation rates relative to other organisms tested. The iron-reducing bacteria, *Shewanella oneidensis* and *Geobacter sulfurreducens* both showed similar initial uptake rates and specificities for Hg-thiol complexes with some thiol ligands, such as cysteine, enhancing uptake and other thiols such as penicillamine or glutathione inhibiting uptake. In contrast, the sulfate-reducing bacterium, *Desulfovibrio* sp. ND132, isolated from highly sulfidic estuarine waters, had the highest affinity for Hg thiol complexes and was able to take up Hg bound to a variety of thiols, including both penicillamine and glutathione, neither of which support Hg uptake in iron-reducing bacteria. These results demonstrate differences in Hg bioavailability across taxa and respiratory guild. Data obtained from this study is critical for understanding how different populations respond to changing Hg speciation in order to better predict methylmercury accumulation in the environment.

## Genomic and synchrotron based investigation of metal immobilization during fermentation-supported sulfate reduction

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*University-Led Research*

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Subsurface and bioreactor systems containing an abundance of solid organic substrates offer a rich environment in which to study the influence of microbial ecology on sulfide-driven metal immobilization. These syntrophic systems rely on cellulolytic and saccharolytic fermenters to metabolize lignocellulosic materials into small organic acids and alcohols. Resulting soluble products are in turn utilized as electron donors by sulfate-reducing bacteria (SRB) who produce sulfide that can react with soluble contaminants such as zinc, copper and nickel to form insoluble metal-sulfides. In this research, we employed seven ex situ pilot-scale and six lab-scale sulfate-reducing bioreactors amended with different solid substrate permutations that received circumneutral, Zn-laden mining-impacted water. Next generation sequencing was used in conjunction with multivariate statistics to identify temporal and spatial phylogenetic trends with the ability to correlate to metabolic drivers of community composition. Despite conservation in the overall organoheterotrophic community across substrate permutations (varying percentages of woodchips and alfalfa) results indicated more recalcitrant lignocellulosic substrates selected for higher ratios of bacteroidetes to firmicutes as well as less pronounced sulfate reduction and Zn immobilization. *Ruminococcus sp.* and *Dysgonomonas sp.*, frequently linked to cellulose and cellobiose fermentation, were present in all columns regardless of substrate, although *Ruminococcus sp.* was preferentially correlated with woodchip content. In contrast, *Treponema sp.* was predominantly encountered in alfalfa-containing columns. Synchrotron-based analysis revealed geochemical patterns where Zn and Ni correlated spatially with S, indicative of sulfide-driven metal immobilization. S-speciation analysis was also used to differentiate between metal-bound sulfide, sulfate associated with metals, and organically bound sulfate. In addition, metallo-labeling of specific microbial genera using biotinylated 16S rRNA targeted DNA-probes, followed by incubation with a streptavidin-nanogold conjugate and subsequent gold-enhancement (Gold-FISH) was improved by targeting multiple ribosomal sites, thus significantly increasing the signal to noise ratio without severely affecting the redox chemistry of the microbe-mineral interface.

The natural environment of *Geobacter sulfurreducens* is oligotrophic and described as limiting in both electron donors and terminal electron acceptors (TEA). We examine here long-term batch cultures under limiting electron donors or the TEAs. The microorganism survived under long-term electron donor (acetate) starvation, maintaining a stable population of  $\sim 1-2 \times 10^8$  cells mL<sup>-1</sup> for >650 days. Proteins that varied in abundance with a high level of statistical significance ( $p < 0.05$ ) for stages between mid-log to survival phase (acetate starved) were identified using mass spectroscopy. The most highly represented proteins that significantly increased in level in the survival phase cells are generally membrane-associated and are involved in energy metabolism and protein fate. These results document that changes in the outer and cytoplasmic membranes help *G. sulfurreducens* survive during starvation through detection and transport of nutrients into the cell. A sizeable portion of the identified proteins with unknown or hypothetical function further suggest that much of the biological process involved in survival have yet to be fully understood. *G. sulfurreducens* was also able to survive under long-term TEA-starvation conditions with iron citrate as TEA and maintained a stable population of  $1.5-3 \times 10^7$  cells mL<sup>-1</sup> for >650 days. We also found that survival phase cells from fumarate-limiting conditions were able to quickly resuscitate and reduce metal such as ferric iron as compared to the mid-log phase cells.

# **University Abstracts: TES Oriented**

## **Carbon Dynamics of Forest Recovery under a Changing Climate: Forcings, Feedbacks, and Implications for Earth System Modeling**

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Regenerating forests make major contributions to the global carbon (C) cycle, and understanding how global change will alter patterns of regeneration and C storage will be necessary to predict the rate of atmospheric CO<sub>2</sub> increase in future decades. We are using a combination of data synthesis and modeling to understand how C cycling in forests varies as a function of ecosystem age, how these patterns vary globally with respect to climate, and how expected changes in atmospheric CO<sub>2</sub> and climate will impact the long-term dynamics of forest regrowth.

To advance understanding of patterns of the C dynamics of forest recovery, we are compiling a new database, the Forest C database (ForC-db), which contains data on C stocks and fluxes in forest ecosystems along with each site's disturbance history. This database contains >14,000 records from >1,400 stands, making it the largest and most comprehensive database on ground-based measurements of C stocks and flows in forest ecosystems globally. Using the tropical component of ForC-db (TropForC-db; >2,200 records from >445 stands), we show that the rate of biomass accumulation in regenerating tropical forests is jointly shaped by climate and disturbance history. Specifically, forest regeneration is faster in everwet than in seasonal climates, slower following cultivation or grazing than other disturbance types, and faster in planted than in naturally regenerating forests. We expect that this database will prove useful for model evaluation and for quantifying the contribution of secondary forests to the global C cycle.

To understand how elevated CO<sub>2</sub> and climate change affect the long-term dynamics of forest regrowth, we are modeling the dynamics of forest recovery using the mechanistic size- and age-structured Ecosystem Demography model (ED2). We have applied the model to Duke Forest, drawing upon data from the FACE experiment, age chronosequence, and eddy flux towers for model parameterization and evaluation. We show that elevated CO<sub>2</sub> is likely to increase the rate of biomass accumulation and community turnover and to alter the successional pathway and mature forest composition. Model predictions of mature forest biomass and ecosystem-atmosphere exchange of CO<sub>2</sub> and H<sub>2</sub>O are sensitive to assumptions about nitrogen limitation; both the magnitude and persistence of the ecosystem response to elevated CO<sub>2</sub> are reduced under N limitation. Regardless, our model simulations demonstrate that elevated CO<sub>2</sub> will result in a general acceleration of forest regeneration while altering the course of successional change and having a lasting impact on forest ecosystems.

## Initial Responses of Methane Cycling to Deep Peat Warming in a Minnesota Bog

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Northern peatlands store roughly one-third of terrestrial soil carbon and are responsible for a significant fraction of the global flux of the potent greenhouse gas CH<sub>4</sub> to the atmosphere. A pressing question in global biogeochemistry remains whether warming will enhance the release of CO<sub>2</sub> and/or CH<sub>4</sub> from this massive soil carbon pool. A mechanistic answer to this question is necessary for Earth system models to accurately predict ecosystem-climate feedbacks in response to ongoing global change. The Spruce and Peatland Responses Under Climatic and Environmental Change (SPRUCES) project will ultimately manipulate temperature (+0, +2.25, +4.5, +6.75 and +9 °C) and atmospheric CO<sub>2</sub> concentrations (Ambient, +850 ppmv) within a northern Minnesota bog. Warming through the entire ~2 m peat profile was initiated in June of 2014, allowing for the unique exploration of the impact of in situ deep warming on carbon mineralization dynamics in this peatland. In September 2014, soil cores were collected at 25, 50, 100, and 200 cm depths from each experimental plot at the SPRUCES site and anaerobically incubated at in situ temperatures with a <sup>14</sup>CO<sub>2</sub> tracer to measure rates of hydrogenotrophic CH<sub>4</sub> production, with rates of acetoclastic methanogenesis determined by difference from total CH<sub>4</sub> production. The CH<sub>4</sub>, CO<sub>2</sub>, and CH<sub>4</sub>:CO<sub>2</sub> temperature responses varied by depth (p = 0.002), with surface peat being more responsive to temperature than deeper peat. Additionally, the proportion and rate of acetoclastic methanogenesis significantly increased with temperature in surface peat (rates were below the detection limit in deeper peat). However, warming had no impact on the concentration and isotopic signature of porewater CH<sub>4</sub> through the peat profile. While SPRUCES will continue for many years, our initial results suggest that the vast carbon stores at depth in peatlands will be less responsive to warming than surface peat. Moreover, shifts in the CH<sub>4</sub> production pathway reveal that increased warming can cause changes in microbial community dynamics in as little as three months. Finally, we have compared CH<sub>4</sub> cycling in the S1 Bog (the home of the SPRUCES project) to two other *Sphagnum* moss-dominated peatlands in the region to highlight differences in the controls of CH<sub>4</sub> cycling - and the potential for different responses to warming - even within bog-like northern peatlands.

## **Dynamic effects of hydraulic redistribution on nutrient availability and ecosystem carbon pools.**

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Hydraulic redistribution (HR) of soil water by plant root systems occurs in seasonally dry ecosystems worldwide. Using measurements and modeling, we are exploring small- and large-scale effects of HR on soil water content throughout the soil column, decomposition and microbial activity, and net ecosystem carbon and energy exchange, in seasonally dry ecosystems of the Western U.S.

At the single root scale, using MIN3P, we have modeled a 10-cm radial soil domain, with root at center, and simulated solute transport, soil cation exchange, and root nutrient uptake under two water flow patterns: daytime transpiration alone, and daytime transpiration with nighttime HR. We find that daytime transpiration leads to the accumulation of cations in the rhizosphere. Some of these cations accumulate to high concentration if not taken up by roots (e.g. calcium, magnesium, and sodium); the cessation of transpiration at night allows these cations to diffuse back out into soil where they outcompete and release ammonium ( $\text{NH}_4^+$ ) and potassium ( $\text{K}^+$ ) from soil cation exchange sites, generating hotspots of  $\text{NH}_4^+$  and  $\text{K}^+$  availability ~0.5 cm from the root. Hydraulic redistribution, releasing water from roots at night, intensifies the effect, but also flushes mobile nutrients away from roots.  $\text{NH}_4^+$  hotspot generation depends on both CEC and flow, and may influence root-microbial competition belowground and microbial food webs.

At the ecosystem scale, we folded Ryel et al.'s (2002) HR formulation into CLM4.5 and examined how well the combined model simulated measured evapotranspiration and the vertical profile of soil moisture, at eight seasonally-dry Ameriflux sites in Washington, Arizona, and California. We extended the analysis to incorporate Ryel's HR formulation into CLM4.5-BGC, to investigate effects of HR on net ecosystem exchange of carbon (NEE), net primary productivity, and plant and soil carbon pools. Preliminary results suggest that at the Washington Wind River Crane (US-Wrc) site, HR-associated changes in NEE mainly occurred during dry periods; CLM4.5 alone strongly overestimated NEE during drought, whereas modeled CLM4.5+HR matched observed NEE more closely. At US-SRM, HR-associated changes in NEE occurred throughout the year. At both sites, modeled soil carbon storage was increased by inclusion of HR, as were multiple plant carbon pools (LAI, leaf and stem and root C).

Molly Cavaleri

Tropical Response to Altered Climate Experiment (TRACE): adventures in warming a wet tropical forest in Puerto Rico

Although tropical forests account for only a fraction of the planet's terrestrial surface, they exchange more carbon dioxide with the atmosphere than any other biome on Earth, and thus play a disproportionate role in the global climate. In the next 20 years, the tropics will experience unprecedented warming. With a Coupled Model Intercomparison Project Phase 5 analysis, we found that model variability in projected net ecosystem production was nearly 3 times greater in the tropics than for any other latitude, thus showing exceedingly high uncertainty in projected tropical responses to this imminent climatic shift. Through a review of the most current literature, we concluded that manipulative warming experiments are vital to accurately predicting future tropical forest carbon balance. Our preliminary data from a wet tropical forest canopy in Puerto Rico shows that photosynthetic optima already exceed maximum leaf temperatures, indicating a decline in carbon assimilation at mid-day temperatures which may be exacerbated by further warming. Yet, it is unknown to what extent tropical species will be able to acclimate, thus mitigating this trend of decreasing the carbon sink behavior of tropical forests. To address these critical research needs, we introduce our Tropical Response to Altered Climate Experiment (TRACE), newly installed in a wet tropical forest in Puerto Rico (El Yunque National Forest). Our primary objectives are: 1) to investigate thermal acclimation potential of mature tropical tree canopy foliage physiology using canopy access towers, branch warming techniques, and chamber gas exchange measurements, and 2) to assess the effects of warming on carbon and nutrient cycling and storage in tropical forest soils with a field warming experiment: the first of its kind in any tropical forest. Results of this research will ultimately represent a significant step forward in our understanding and ability to effectively model tropical forest responses to a warmer world.

Throughout the southern US, past forest management practices have replaced large areas of native forests with loblolly pine plantations and have resulted in changes in forest response to extreme weather conditions. However, uncertainty remains about the response of plantation versus natural species to drought across the geographical range of these forests. Taking advantage of a cluster of unmanaged stands (85-130 year-old hardwoods) and managed plantations (17-20 year-old loblolly pine) in coastal and Piedmont areas of North Carolina, tree water use, cavitation resistance, whole-tree hydraulic ( $K_{tree}$ ) and stomatal ( $G_s$ ) conductances were measured in four sites covering representative forests growing in the region. We also used a hydraulic model to calculate natural versus plantation transpiration and the resilience to extreme soil drying. Our objectives were to determine: (1) if  $K_{tree}$  and stomatal regulation in response to atmospheric and soil droughts differ between species and sites; (2) how ecosystem type, through tree water use, resistance to cavitation and rooting profiles, affects the water uptake limit that can be reached under drought; and (3) the influence of stand species composition on critical transpiration that sets a functional water uptake limit under drought conditions. The results show that across sites, water stress affected the coordination between  $K_{tree}$  and  $G_s$ . As soil water content dropped below 20% relative extractable water,  $K_{tree}$  declined faster and thus explained the decrease in  $G_s$  and in its sensitivity to vapor pressure deficit. Compared to branches, the capability of roots to resist high xylem tension has a great impact on tree-level water use and ultimately had important implications for pine plantations resistance to future summer droughts. Model simulations revealed that the decline in  $K_{tree}$  due to xylem cavitation aggravated the effects of soil drying on tree transpiration. The critical transpiration rate ( $E_{crit}$ ), which corresponds to the maximum rate at which transpiration begins to level off to prevent irreversible hydraulic failure, was higher in managed forest plantations than in their unmanaged counterparts. However, even with this higher  $E_{crit}$ , the pine plantations operated very close to their critical leaf water potentials (i.e. to their permissible water potentials without total hydraulic failure), suggesting that intensively managed plantations are more drought-sensitive than unmanaged stands.

Key words: cavitation, drought, natural stands, pine, plantations, transpiration

**Title:** What Regulates the Seasonality of Photosynthetic Metabolism in Tropical Forests?

**Program:** TES

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**Abstract:**

This U.S-Brazil collaboration investigates a basic yet unanswered question in Earth system and global carbon cycle science: what controls the response of photosynthesis in Amazon tropical forests to seasonal variations in climate? This question, despite its apparent simplicity, is the subject of an ongoing scientific puzzle that has so far been remarkably difficult to solve with confidence. For example, seasonal patterns of photosynthesis simulated by several state-of-the-art, computer-based models of the Earth system disagree with seasonal patterns seen in vegetation “greenness” recorded by Earth-observing satellites, and with measurements of ecosystem-atmosphere carbon dioxide exchange at monitoring sites in the central Amazon. The project is designed to resolve these disagreements by developing new knowledge and deeper understanding of seasonal climate-photosynthesis relations in tropical forests of the Brazilian Amazon, across a gradient of dry season length between Manaus (with a short dry season) and Santarem (with a long dry season). We use intensive field campaigns to measure physiological and ecohydrologic properties of leaves and trees, innovative remote sensing instruments to monitor forest optical properties and the effects of clouds and smoke on solar radiation, and photosynthesis modeling that accounts for 3-dimensional variation in the forest structure and light environment to guide improvements in the treatment of tropical forest photosynthesis in Earth system models, and help establish a foundation for the planned Next Generation Ecosystem Experiments (NGEE) in the Tropics. Our initial findings suggest that biological factors, specifically the canopy-scale composite of leaf ontogeny (age-dependent physiology) and demography (the distribution of age across different cohorts of leaves) can successfully reconcile disparate patterns of central Amazon forest seasonality observed from eddy flux towers and satellites. Our related, preliminary findings provide additional insights on what regulates the seasonality of photosynthetic metabolism in tropical forests by illustrating tree-to-patch-scale relationships between growth, water flow, and the hydraulic state of the canopy.

## **Exploring the Influence of Topography on Belowground C Processes at the Shale Hills Critical Zone Observatory**

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Belowground carbon processes are strongly affected by soil moisture and soil temperature. Current studies are generally limited to sites with relatively uniform topography, and seldom connect the impacts of natural variation in soil moisture associated with topography to multiple C cycle processes. Likewise, current biogeochemical models are 1-D and cannot resolve topographically driven hill-slope soil moisture patterns, and cannot simulate the nonlinear effects of soil moisture on carbon processes. In this project we will assess the influence of topography on multiple belowground processes (soil CO<sub>2</sub> efflux, soil C, microbial biomass, root density, root production, and root turnover) and develop a coupled modeling system capable of simulating the water and carbon dynamics of this complex system.

A spatially distributed forest ecosystem model has been developed by coupling a 1-D mechanistic biogeochemistry model Biome-BGC (BBGC) with a spatially distributed land surface hydrologic model, Flux-PIHM. Flux-PIHM is a coupled physically based model, which incorporates a land-surface scheme into the Penn State Integrated Hydrologic Model (PIHM). The land surface scheme is adapted from the Noah land surface model. Because PIHM is capable of simulating lateral water flow and deep groundwater, Flux-PIHM is able to represent the link between groundwater and the surface energy balance, as well as the land surface heterogeneities caused by topography. In the coupled Flux-PIHM-BBGC model, each Flux-PIHM model grid couples a 1-D BBGC model. Flux-PIHM provides BBGC with soil moisture and soil temperature information, while BBGC provides Flux-PIHM with leaf area index.

The coupled Flux-PIHM-BGC model has been implemented at the Susquehanna/Shale Hills critical zone observatory (SSHCZO). Preliminary results show that the Flux-PIHM-BBGC simulated soil carbon pool shows clear impact from topography. The simulated vegetation carbon pool is mainly affected by vegetation type.

We have collected root length density at 250 sites in the Shale Hills catchment to a maximum depth of 165 cm. Initial results show relatively modest differences in root distribution by depth based on topographic position at the site. Soil analysis from each core sample is currently being processed. The combination of root and soil measurements will also be used as important input parameters and calibration and evaluation data for the Flux-PIHM-BGC model.

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## **Title: Spatial Variation in Microbial Processes Controlling Carbon Mineralization within Soils and Sediments**

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Approximately 3300 Pg of carbon (C) are stored in soils as organic matter, which is three-times the amount stored in the atmosphere. An important control on soil organic matter (SOM) storage is the mineralization (oxidation) rate, which is affected by climatic factors (particularly temperature and rainfall) influencing microbial metabolic rates as well as SOM chemistry, mineral-organic associations, and physical protection. What remains elusive is to what extent constraints on microbial metabolisms induced by the respiratory pathway, and specifically the electron acceptor in respiration, control overall rates of carbon mineralization in soils. The complex physical structure of soils and sediments results in an abundance of redox environments even within seemingly aerobic systems. Therefore, factors limiting oxygen diffusion and availability such as soil texture and aggregate size (soil structure) may be central controls on microbial C mineralization rates. Here, we are combining laboratory studies with in-field measurements to examine if soil structure and carbon availability interact to impose respiratory constraints on organic matter mineralization rates and thus storage.

In model aggregates, we determined the distribution of operative microbial metabolisms and their cumulative impact on SOM transformations and overall oxidation rates across soil redox gradients. In both saturated and unsaturated systems, microsensor measurements in combination with gas flux measurements showed that particle size exerts a strong control on the extent of the anaerobic volume, thereby causing an overall decrease in OM oxidation rates. Density separations and C 1s NEXAFS spectroscopy showed that the formation of persistent anaerobic microsites resulted in the preferential preservation of reduced (electron-rich) organic carbon compounds (both dissolved and particulate), a result corroborated by field measurements across multiple sites. Metabolic profiling showed that volume-specific aerobic respiration rates are an order of magnitude larger than those for anaerobic respiration, with Fe reduction contribution more than 75% of the overall metabolism. However, our results also indicate that diffusion limitations imposed by small particle sizes not only negatively impacted aerobic respiration but also anaerobic respiratory pathways, suggesting that the predictive power of ‘soil texture’ used in current soil C cycling models may not only be grounded in mineral protection mechanisms, but also in diffusion limitations creating anaerobic microsites. Collectively, our results suggest that anaerobic microsites are an underappreciated OM protection mechanism in soils (upland and lowland). Because this mechanism appears to be most important for organic carbon compounds thought to be inherently available for microbial catabolism, it may be particularly vulnerable to changes in environmental conditions due to climate change.

## Canopy Spectral Imaging (NDVI) As A Proxy Measurement Of Shrub Biomass And Ecosystem Carbon Fluxes Across Arctic Tundra Habitats

C.E. Flower, J.M. Welker, M. Anderson-Smith, N. E. Van Hoey, C.J. Whelan, and M.A. Gonzalez-Meler

There is widespread consensus that climate change is contributing to rapid vegetation shifts in the ecologically sensitive Arctic tundra. These tussock grass dominated systems are shifting to tussock/woody shrub communities leading to likely alterations in carbon sequestration and ecosystem productivity, which in turn can manifest in “greening” and changes in normalized difference vegetation index values (NDVI). While the expansion of woody vegetation is well established, our understanding of the ecosystem dynamics associated with this new habitat remain largely unknown. To untangle how the Arctic tundra may be impacted by these vegetation shifts we paired vegetation measurements (*i.e.* shrub biomass, leaf area, and shrub canopy area) and ecosystem carbon fluxes (*e.g.* net ecosystem exchange, NEE, and ecosystem respiration) with ground-level measurements of NDVI. We conducted these measurements at the Toolik Field Station in dry heath and moist acidic tundra habitats which are representative of the primary habitat types on the North Slope of Alaska. We found strong positive relationships between shrub leaf area and shrub biomass as well as shrub canopy area and shrub biomass, relationships that were corroborated with NDVI measurements ( $R^2=0.6$ ;  $P=0.01$ ). This lends support for the use of NDVI as a proxy measurement of not only leaf area but also shrub biomass. Additionally, NDVI was negatively correlated with ecosystem respiration across habitats, with respiratory fluxes consistently higher in the moist acidic tundra relative to the dry heath tundra. Finally, we observed a significant positive relationship between net ecosystem exchange and NDVI ( $R^2=0.7$ ;  $P<0.01$ ). The positive relationship between NDVI and NEE highlights the potential shifts in the carbon balance of the Arctic tundra associated with an increased prevalence of woody vegetation. This increased plant productivity may offset greenhouse gas losses from permafrost degradation contributing some resilience to this system otherwise considered a considerable carbon source. Such ground-truthed relationships can facilitate assessments of long-term trends in NDVI and their ramifications on ecosystem C cycling processes. These relationships will enhance our ability to predict shifts in standing carbon mass, carbon cycling, and use historic satellite products to assess change.

## **Effects of Experimental Warming and Elevated CO<sub>2</sub> on Trace Gas Emissions from a Black Spruce Peatland [SPRUCE]**

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### **Objective and Methods**

The objective of this research is to quantify the fluxes and isotopic compositions of CO<sub>2</sub> and CH<sub>4</sub> from a black spruce peatland exposed to experimental warming and elevated concentrations of atmospheric CO<sub>2</sub>. This research contributes to the DOE-funded SPRUCE project whose overarching goal is to determine how the C balance of high latitude ecosystems will change in response to climatic and atmospheric change. Our core research is comprised of autochamber measurements during the growing season. Alongside chamber-specific temperature, moisture and O<sub>2</sub> concentrations this research will identify environmental drivers of these fluxes. The isotopic compositions of the C-based trace gasses will inform biotic regulation of trace gas emissions

### **Results and Conclusions**

This project was funded in the spring of 2014. This past growing season we quantified the fluxes and isotopic compositions of CO<sub>2</sub> and CH<sub>4</sub> in response to peat warming at 2-m depth. During this growing season we made manual measurements in the early growing season before warming was initiated (June), in midsummer during the heat accumulation period (July), and at the end of the growing season after all treatments reached target temperature differentials (Sept). During this first year of partial treatments [see below], CH<sub>4</sub> flux was consistently higher in hollow compared to hummock microtopographic positions and increased in response to warming up to 9 °C. At present the isotopic composition of the CH<sub>4</sub> flux suggests a strongly hydrogenotrophic signature. CO<sub>2</sub> efflux was also higher in hummock compared to hollow microtopographic positions. CO<sub>2</sub> efflux also increased with increasing temperature but only late in the growing season once deep peat reach target temperature.

This past fall and winter we designed and built automatic soil respiration of CH<sub>4</sub> efflux chambers that will be deployed in May 2015 at the site. Two autochambers will be located in each experimental plot and will operate from May through September (N=20). These [beautiful] chambers will substantially increase temporal data density and enable us to assess diurnal to seasonal scale variations in fluxes in response to experimental treatments. Spring 2015 will not only have deep-peat heating but also surface heating and elevated CO<sub>2</sub>; the replicated experiment will be fully operational. The data collected over the next several growing seasons will be used to calibrate a model of exoenzyme activity and microbial physiology [MCNiP, Finzi et al. 2015].

Title: How does the definition of plant functional types affect the modeling of carbon and water fluxes on a mixed pine/oak forest?

Authors: Renato P.M. Frasson, Golnazalsadat Mirfenderesgi, Gil Bohrer, Karina V.R. Schäfer

Abstract:

Land surface models reduce computations by resolving energy, water, and nutrient balances of representative vegetation groups instead of operating on individual trees. Such groups are often based on plant functional type (PFT) and tree size or age. The group's plant functional type dictates which parameters control plant physiology while, in some demographic models, age or size of each cohort defines their access to different resources. Our work examines the sensitivity of ecosystem fluxes to the resolution and definition of PFTs in an Atlantic Coastal Plain upland forest. Our study site is located in the Northeastern USA, at the Rutgers Pinelands Research Station (USFS Silas Little Experimental Forest), in New Jersey, USA. Species in the site include chestnut oak (*Quercus prinus*), black oak (*Quercus velutina*), scarlet oak (*Quercus coccinea* Muenchh.), white oak (*Quercus alba* L.), post oak (*Quercus stellata* Wangenh.), pitch pine (*Pinus rigida* Mill.) and shortleaf pine (*Pinus echinata* Mill.). Previous experimental works conducted at this site identified two distinct water-use strategies among the local oak species. While one group has higher Rubisco-limited carboxylation rate ( $V_{\text{cmax}}$ ), it requires more water than the second group, which has a more conservative nutrient and water use strategy. We employ the Ecosystem Demography model version 2 (ED2) to test two different scenarios. In the first, we utilize ED2's standard definition of plant functional types, classifying all oaks as temperate, mid-successional deciduous trees and the pines as northern pines. In the second scenario, we create two distinct plant functional types to describe the oak species. The first oak PFT has higher Rubisco-limited carboxylation rate ( $V_{\text{cmax}}$ ), higher dark respiration rate, and lower water availability parameter ( $K_w$ ). The second PFT has higher  $K_w$ , lower  $V_{\text{cmax}}$ , and lower dark respiration rate. We evaluate our estimates of carbon and water fluxes against eddy covariance data collected at the Silas Little Experimental Forest. As a result of our work, we expect to determine if grouping of oak species with different water usage strategies into one plant functional type is detrimental to our ability to predict plot level water and carbon fluxes.

Peat is a large reservoir of stored carbon and peat cores preserve a long-term record of system carbon and nitrogen dynamics. Stable isotopes are one marker of carbon and nitrogen dynamics in peat cores. Here, we investigated controls over  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  patterns in peat cores from the Marcell S1 forested bog in northern Minnesota. In multiple regression analyses,  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  correlated strongly with depth, plot location, %C, %N, and each other. Negative correlation of  $\delta^{15}\text{N}$  with %N presumably reflected removal of  $^{15}\text{N}$ -depleted N via denitrification, diffusion, or plant N transfer via mycorrhizal fungi. The step increase in the depth coefficient for  $\delta^{15}\text{N}$  of  $\sim 3\text{‰}$  from -25 cm to -35 cm indicated that the removal process primarily operates at a discrete depth, presumably corresponding to the juncture between aerobic and anaerobic layers defined by the water table. Variability of  $\delta^{15}\text{N}$  with plot location in the raised bog may reflect flowpath alterations derived from proximity to uplands. The Suess effect and aerobic decomposition lowered  $\delta^{13}\text{C}$  in recent surficial samples. Small increases in  $\delta^{13}\text{C}$  at -112 cm (4290 calibrated years BP) and -85 cm (3820 calibrated years BP) may reflect warming of about  $1^\circ\text{C}$  during a suspected transitional fen stage (based on paleoecology at a nearby bog). Alternatively, these increases may reflect a signal of carbon dynamics during this stage, when reduced methanotrophy would have retained less  $^{13}\text{C}$ -depleted carbon derived from methane. C/N decreased until about -85 cm and thereafter remained steady, suggesting that the active zone of aerobic processing during drought may extend to this depth.

Abstract title: Carbon Dynamics of the Greater Everglades Watershed and Implications of Climate Change

We continued Eddy covariance (EC) tower measurements for CO<sub>2</sub>, H<sub>2</sub>O, and CH<sub>4</sub> along a hydrologic gradient at three sites: longleaf pine flatwoods (CO<sub>2</sub> and H<sub>2</sub>O only), seasonally inundated depression marsh, and peat accumulating sawgrass marsh (Blue Cypress). Selected findings to date include:

- Blue Cypress marsh has been a sink for CO<sub>2</sub> in all measurement years.
- Eddy flux measurements interannual variability in net ecosystem exchange (NEE) of CO<sub>2</sub>, which ranged from -72 g C m<sup>-2</sup> to -602 g C m<sup>-2</sup>, was driven largely by hydroperiod, mainly as a result of increased peat oxidation during dry periods.
- A fire in March 2014 released 963±165 g C. Photosynthesis was reduced immediately following fire, but recovered within 1-2 months.
- Methane emissions were 44 g C m<sup>-2</sup> in 2013. Considering that 1 ton CH<sub>4</sub> has a Greenhouse Gas (GHG) equivalence of 24 tons of CO<sub>2</sub>, CH<sub>4</sub> emissions may negate the benefit of CO<sub>2</sub> sequestration.
- Based on the assumption that dry years occur 30% of the time and a fire return interval of 6 years, long-term C sequestration within the marsh would average ~150 g C m<sup>-2</sup> y<sup>-1</sup>.

In addition to the eddy covariance measurements, transects were established at all sites for chamber measurements of NEE. Closed-chamber carbon exchange over a range of light conditions was conducted at all three sites as well as along an ecotonal transect at a small depression marsh within the pine flatwoods tower fetch. Additionally at the sawgrass marsh, leaf gas exchange (photosynthesis and transpiration) is being monitored for sawgrass and willow to evaluate the impact of wetland shrub encroachment on landscape water and carbon cycling. A new effort to partition methane production, oxidation, and transport along the soil-atmosphere continuum has been initiated.

Ground Penetrating Radar (GPR) surveys focused on two studies related to carbon dynamics: 1) to estimate the contribution of depression wetlands as carbon stocks at the pine flatwoods and depression marsh sites; and 2) to investigate the spatial variability of biogenic gas releases from peat monoliths from the three study sites at the laboratory scale. In the first case 3D GPR surveys were combined with direct coring and carbon content analysis to estimate total carbon content as based on peat volume estimates along depression wetlands, and satellite imagery were used to upscale estimates beyond the plot scale. In the second case time-lapse GPR was combined with gas traps and time-lapse cameras to investigate biogenic gas dynamics (i.e. methane and carbon dioxide build-up and release) in samples from all three study sites along the hydrological gradient. Future work with the GPR will include exporting this approach to the field site in order to investigate in-situ gas dynamics at the three study sites.

## Peatland topography influences microbial function at SPRUCE

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Microbial activities are central for modeling soil carbon (C) and nitrogen (N) cycling because microorganisms release extracellular enzymes to decompose soil organic matter (SOM) and produce bioavailable C and N. However, scaling microbial traits, such as biomass or enzyme potentials, is challenging, particularly in boreal wetlands, which are vulnerable to shifting climate, and spatially complex due to micro-topographic features. Characterizing spatial variability in microbial traits can improve our ability to detect and accurately scale microbial mechanisms that influence C and N cycling. To quantify the spatial variation and functional characteristics related to microbial decomposition of peat organic matter, we measured microbial traits along a micro-topographic gradient at the Spruce and Peatland Responses Under Climatic and Environmental Change Experimental (SPRUCE) site in the Marcell National Forest, Minnesota, USA. Fresh peat cores were collected from hummocks and hollows from 0 to 20 cm below hollow surface at the beginning (June) and the end (September) of the 2013 growing season. Fungal community composition, microbial biomass and potential extracellular enzyme activities were assayed at 10 cm increments. We found that depth and topography were central drivers of differences in microbial biomass and activity, while seasonality influenced fungal community membership. While the majority of microbial biomass resides in the surface of hummocks, at equivalent peat depths, microbial biomass was higher in hollows compared to hummocks, with greatest concentrations in September. Higher microbial biomass coincided with greater polypeptide-degrading enzymes in hollows in both June and September, while carbon cycling enzymes were greater in hollows only in September. Differences in enzyme activity were not supported by changes in fungal community composition (relative OTU abundance) across topography, depth, or season, suggesting that shifts in bacterial community composition or physiological responses may be driving differences in microbial function. Together these results demonstrate how consideration of micro-habitats within the peatland provides greater resolution for understanding the biological responses driving ecosystem scale biogeochemistry.

## Partitioning autotrophic and heterotrophic respiration at Howland Forest

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Terrestrial ecosystem respiration is the combined flux of CO<sub>2</sub> to the atmosphere from above- and below-ground, plant (autotrophic) and microbial (heterotrophic) sources. Flux measurements alone (e.g., from eddy covariance towers or soil chambers) cannot distinguish the contributions from these sources, which may change seasonally and respond differently to temperature and moisture. The development of improved process-based models that can predict how plants and microbes respond to changing environmental conditions (on seasonal, interannual, or decadal timescales) requires data from field observations and experiments to distinguish among these respiration sources.

We tested the viability of partitioning of soil and ecosystem respiration into autotrophic and heterotrophic components with different approaches at the Howland Forest in central Maine, USA. These include an experimental manipulation using the classic root trenching approach and targeted  $\Delta^{14}\text{CO}_2$  measurements. For the isotopic measurements, we used a two-end member mass balance approach to determine the fraction of soil respiration from autotrophic and heterotrophic sources. When summed over the course of the growing season, the trenched chamber flux (heterotrophic) accounted for  $53 \pm 2\%$  of the total control chamber flux. Over the four different <sup>14</sup>C sampling periods, the heterotrophic component ranged from 35-55% and the autotrophic component ranges 45-65% of the total flux.

Our next step is to assess the value of the flux partitioning for constraining a simple ecosystem model using a model-data fusion approach to reduce uncertainties in estimates of NPP and simulation of future soil C stocks and fluxes.

## IMPROVING MODELS TO PREDICT PHENOLOGICAL RESPONSES TO GLOBAL CHANGE

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Vegetation phenology, the environmentally-mediated timing of recurrent plant lifecycle events, is both a sensitive indicator of climate change and a forceful influence on it. However, despite the robustness of phenological indicators and the central role of biosphere-atmosphere feedbacks in the global carbon cycle, existing phenology models tend to produce biased predictions, typically neglecting the possible influence of CO<sub>2</sub> concentrations. Manipulative global change experiments and long-term observational data are required to advance mechanistic understanding and prediction of vegetation phenology in the face of climate change.

This research will combine two independent datasets – experimental and observational – to model, validate, and predict the phenological response of boreal peatland forests to global change. The experimental dataset will be comprised of near-surface remote sensing imagery from Oak Ridge National Laboratory’s Spruce and Peatland Responses Under Climatic and Environmental Change (SPRUCE) site in northern Minnesota. When construction is completed this summer, open-topped chambers at SPRUCE will be subjected to one of five warming levels (ambient to +9.0°C) and ambient or elevated (800 ppm) CO<sub>2</sub> concentrations. Chamber-mounted cameras will capture digital images of vegetation every 30 minutes, and we will use the image color channels to calculate a quantitative measure of phenological transitions. Observational data are from Mr. John Latimer, a rural postal deliveryman from northern Minnesota who recorded dates of flowering, budburst, and leaf-off for over 30 plant species along his mail route for the past three decades. Specifically, we are using these datasets to (1) elucidate environmental drivers of multi-species phenological transitions in a boreal peatland forest ecosystem and (2) incorporate mechanistic understanding of drivers into models predicting peatland forest phenological response to climate change.

Preliminary analysis of Mr. Latimer’s data focusing on 15 of the most common N. Minnesotan woody species demonstrates species’ differential temperature sensitivity and year-to-year phenological variability. On average, budburst of all 15 species advanced with increasing mean spring temperature (March-May). The median rate of advancement was 2.8 days per degree Celsius (d/°C). Trembling aspen budburst was the most temperature sensitive, advancing an average of  $4.5 \pm 0.57$  d/°C (regression slope  $\pm$  standard error), while paper birch was least sensitive and advanced only  $0.50 \pm 1.3$  d/°C. Year-to-year variation in budburst date was 2.7 to 5.0 weeks, and leaf-off date variation was 1.9 to 5.6 weeks. Effects of increasing CO<sub>2</sub> concentrations on phenology are forthcoming but still unclear.

## Initial Responses of Methane Cycling to Deep Peat Warming in a Minnesota Bog

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Northern peatlands store roughly one-third of terrestrial soil carbon and are responsible for a significant fraction of the global flux of the potent greenhouse gas CH<sub>4</sub> to the atmosphere. A pressing question in global biogeochemistry remains whether warming will enhance the release of CO<sub>2</sub> and/or CH<sub>4</sub> from this massive soil carbon pool. A mechanistic answer to this question is necessary for Earth system models to accurately predict ecosystem-climate feedbacks in response to ongoing global change. The Spruce and Peatland Responses Under Climatic and Environmental Change (SPRUCE) project will ultimately manipulate temperature (+0, +2.25, +4.5, +6.75 and +9 °C) and atmospheric CO<sub>2</sub> concentrations (Ambient, +850 ppmv) within a northern Minnesota bog. Warming through the entire ~2 m peat profile was initiated in June of 2014, allowing for the unique exploration of the impact of in situ deep warming on carbon mineralization dynamics in this peatland. In September 2014, soil cores were collected at 25, 50, 100, and 200 cm depths from each experimental plot at the SPRUCE site and anaerobically incubated at in situ temperatures with a <sup>14</sup>CO<sub>2</sub> tracer to measure rates of hydrogenotrophic CH<sub>4</sub> production, with rates of acetoclastic methanogenesis determined by difference from total CH<sub>4</sub> production. The CH<sub>4</sub>, CO<sub>2</sub>, and CH<sub>4</sub>:CO<sub>2</sub> temperature responses varied by depth (p = 0.002), with surface peat being more responsive to temperature than deeper peat. Additionally, the proportion and rate of acetoclastic methanogenesis significantly increased with temperature in surface peat (rates were below the detection limit in deeper peat). However, warming had no impact on the concentration and isotopic signature of porewater CH<sub>4</sub> through the peat profile. While SPRUCE will continue for many years, our initial results suggest that the vast carbon stores at depth in peatlands will be less responsive to warming than surface peat. Moreover, shifts in the CH<sub>4</sub> production pathway reveal that increased warming can cause changes in microbial community dynamics in as little as three months. Finally, we have compared CH<sub>4</sub> cycling in the S1 Bog (the home of the SPRUCE project) to two other *Sphagnum* moss-dominated peatlands in the region to highlight differences in the controls of CH<sub>4</sub> cycling - and the potential for different responses to warming - even within bog-like northern peatlands.

**Toward a predictive understanding of the response of belowground microbial carbon turnover to climate change drivers in a boreal peatland.**

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High latitude peatlands store approximately 1/3 of all soil carbon (C), but wetland-specific processes are generally not included in global climate models. Using advanced analytical chemistry, <sup>14</sup>C and <sup>13</sup>C tracing, and next generation gene sequencing, this project will quantify the response of soil organic matter (SOM) storage and reactivity, decomposition, and the functional diversity of microorganisms to climate change manipulation in peatlands. The project is being conducted at the Marcell Experimental Forest (MEF), northern Minnesota, where the Oak Ridge National Lab (ORNL) has established an experimental site known as Spruce and Peatland Response Under Climatic and Environmental Change (SPRUCE). In collaboration with SPRUCE investigators at ORNL, new insights will be incorporated into the land component of the Community Earth System Model to improve climate projections.

Prior to completion of the SPRUCE climate enclosures, our objectives were to document trends in the dynamics of organic carbon compounds linked to microbial community composition to elucidate the controls of belowground C turnover and the potential responses to warming. Here we focused on molecular-level characterization of dissolved organic matter (DOM) in pore waters from the S1 bog at the MEF. Ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT ICR MS) and 3-dimensional excitation emission matrix spectroscopy with PARAFAC analysis (EEMS-PARAFAC) revealed that DOM characteristics were most unique in the 50 cm depth zone that was previously identified as the zone where maximum decomposition of soil organic matter is occurring. Nitrogen- and sulfur-bearing compounds were highest at intermediate depth and we have identified for the first time the presence of polycyclic aromatic compounds that contain both nitrogen and sulfur heteroatoms. EEMS-PARAFAC data from S1 bog were combined with data from other bogs and fens around the world in the development of a general peatlands model for DOM fluorescence.

Using next generation sequencing of SSU rRNA genes, metagenomics, and in silico prediction of bacterial functional content, we further showed that the vertical stratification in microbial communities paralleled changes in methane dynamics and organic carbon composition. Multiple lines of evidence consistently point to Type I and Type II methanotrophs, especially *Methylomonas* and *Methylocystis*, as the dominant active CH<sub>4</sub>-consuming populations in the surface layers of S1 bog. Microbial diversity and members of Alpha/Gammaproteobacteria decreased in relative abundance with depth, while putative anaerobes in the Deltaproteobacteria and Archaea (including methanogens and other functional guilds) increased. To probe the metabolic potential of abundant Archaea, two near-complete archaeal genomes, affiliated with the Thaumarchaeota and Thermoplasmata, were reconstructed from metagenomic data acquired from deep anoxic peat layers. Archaeal genomes revealed the potential to degrade long chain fatty acids (LCFA) via  $\beta$ -oxidation either by syntrophic interaction with methanogens or by coupling oxidation with anaerobic respiration using fumarate or organosulfonates (enriched in humic-like substances) as a terminal electron acceptor (TEA), a result consistent with recent observations of the importance of organic sulfur in organic matter decomposition based on FT-ICR mass spectral characterization.

## **Passive optical imagery for the rapid determination of above ground biomass and vegetation status in piñon-juniper woodlands**

*Dan J. Krofcheck, Christopher Lippitt, Andy Loerch, and Marcy E. Litvak*

Piñon-juniper (PJ) woodlands, the most expansive biome across the Southwestern US, are on the cusp of an imminent transition in vegetation structure, as piñon pine mortality escalates across the region. In response to considerable climatic stress in the past decade, these woodlands have experienced more mortality in piñon (*Pinus edulis*), due to combination of a weaker hydraulic strategy and increased vulnerability to pests like bark beetles, while the juniper (*Juniperus monosperma*), have largely remained intact. Given the sensitivity of this extensive semi-arid biome to drought and pest pressures, rapid and accurate techniques for monitoring mortality and quantifying the subsequent reallocation of above ground biomass from live to dead pools play a critical role in improving our understanding of how large scale, differential disturbance events impact ecosystem function, and catalyze climate feedbacks at local and regional scales. We have been studying the coupled impacts of drought and pest pressures at a pair of eddy covariance instrumented PJ woodlands in central NM since 2009. In one site, we girdled all of the large piñon to simulate bark beetle driven mortality, and left the other intact as a control. The study area has been experiencing significant drought since 2011, and subsequently mortality of piñon pine in our control site has increased dramatically since 2013.

During the progression of the overstory mortality, intensive ground monitoring campaigns coupled with remote sensing data sets have afforded us a very high resolution look at the distribution of mortality through time. We also acquired 4-band (visible, near-infrared) aerial imagery across the 2,033 ha region surrounding our 4 ha study areas in September of 2014. Using modern structure-from-motion processing techniques, we produced a canopy height model from the imagery at 0.35 cm resolution. This 3D structural data paired with the 1 inch resolution 4-band imagery permits an extremely high resolution look at the height, volume, and vegetation status (live / dead) of the vegetation across the research site. This data set, contextualized further by previously flown waveform lidar and repeated Worldview-2 (2-meter, 8-band imagery) satellite acquisitions, is allowing us to conduct an integrated assessment not only of the evolution of canopy mortality through time, but also the ability of the various remote sensing components involved to contribute to the analysis framework. Here we present the following: 1) high resolution remote sensing and field based maps of the progression of canopy mortality of piñon pine during a 3 year period of severe drought, and 2) crown level biomass estimates for the flux tower fetch through time, binned into standing live and dead pools, and 3) an analysis of how the progression of mortality has altered eddy-covariance energy and carbon fluxes from this PJ woodland. Our overall goal is to use this information to scale up to the region to quantify how continued mortality events will likely alter carbon, water and energy dynamics across the region.

## **Soil moisture constrains subalpine tree seedling physiology, recruitment, and population responses to warming across an elevation gradient**

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The elevational range of subalpine trees is known to be climate sensitive. Shifts in the distribution of trees with climate change are dependent on the demographic processes of recruitment, growth and mortality, which occur over decades to centuries for long-lived species. Chronic and acute physiological responses to climate variability can influence demographic outcomes at both leading and trailing edges of species distributions. We established the Alpine Treeline Warming Experiment at Niwot Ridge, CO, to examine effects of climate warming on seedling physiology and tree recruitment near the lower limit of subalpine forest, at upper treeline, and in the alpine. We used infrared heaters to increase surface temperatures and to lengthen the growing season, and watered some plots to distinguish heating from soil-drying effects. We used long-term demography plot data to quantify adult tree growth and mortality. We integrated this experimental and observational data into spatially explicit demography models to assess impacts of warming on tree population sizes and distributions over time.

Preliminary results show that across three species, survivorship increases with seedling age, as do cold and drought tolerance. Lodgepole pine, which rarely occurs at treeline, is less tolerant of freezing than treeline species (limber pine, Engelmann spruce), and had reduced spring but increased fall cold hardiness with warming. Differences among species in drought tolerance match relative abundances of the species in the treeline ecotone (limber pine most tolerant). Patterns of mortality do not match expectations from microclimate thresholds, suggesting slower-acting growth and carbon balance mechanisms determine survival. In limber pine, we find that low soil moisture and temperature can co-limit carbon accumulation at and above treeline, with warming exacerbating soil water limitations. Recruitment is similarly constrained by a combination of temperature and moisture, with warming reducing recruitment in low elevation forest but not enhancing recruitment at treeline or in the alpine due to water limitations. Preliminary model results indicate century-long lags between the onset of climate changes and tree population establishment in the alpine due to seed limitation and low recruitment. Population growth is also sensitive to summer soil moisture, including in the alpine, suggesting that warming may not always result in upslope range shifts. Finally, we find rapid a decline in Engelmann spruce populations at low elevations due to recruitment failure. Linking field experiments and observations with models of population change provides a novel approach to projecting changes in altitudinal distributions of forest with climate change over time.

Abstract Title: Measurements and modeling of CO<sub>2</sub> concentration and isotopes to improve process-level understanding of Arctic and boreal carbon cycling

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#### TES Program

This project seeks to understand terrestrial ecosystem processes that control the exchanges of CO<sub>2</sub> with the atmosphere on decadal and longer time scales. The approach involves carrying out time series measurements of CO<sub>2</sub> concentration and isotopes and uses these and other datasets to challenge and improve carbon cycle models, including earth system models. A core activity involves continuing measurements of CO<sub>2</sub> concentrations and isotopes from the Scripps CO<sub>2</sub> program from flasks collected at an array of ten stations distributed from the Arctic to the Antarctic. It also involves modeling studies and interpretive work to expand on the recent discovery based on airborne data that the amplitude of the seasonal cycle is cycle has increased by 50 to 60% since 1960 at latitudes north of 40N. This amplitude increase stands out as perhaps the most compelling evidence to date for wide-spread changes in land carbon cycling relevant for global CO<sub>2</sub> balance and climate change. This project focuses on three key questions: 1) How is the amplitude increase related to changes in net carbon flux in boreal and arctic systems? 2) What processes are responsible for the amplitude increase? 3) How can the models be improved to incorporate the relevant processes?

**RESULTS:** As modeling work in support of this project is at early stages, emphasis will be placed on observational results. Updates will be presented of seasonal amplitudes at benchmark stations, including Barrow, Alaska, and Mauna Loa as well as correlation between amplitude trends and climate indices. At Barrow, where large (~35%) amplitude increases since 1960 were reported by Graven et al. (Science, 2013), the seasonal amplitude has remained fairly steady over the past 5 years, roughly matching the record values achieved around 2010, and reinforcing the evidence for large long-term change. Updated results will also be presented on covariation of the seasonal cycles of atmospheric CO<sub>2</sub> and the <sup>13</sup>C/<sup>12</sup>C ratio of CO<sub>2</sub> in the northern extratropics. This covariation can be used to assess large-scale trends leaf-level intrinsic water use efficiency (iWUE) and changes in ratio of CO<sub>2</sub> partial pressure within leaf (C<sub>i</sub>) compared to the free atmosphere (C<sub>a</sub>), and is an important constraint on the causes of the long-term trends in amplitude and land biospheric productivity.

## **Ecophysiological controls on Amazonian precipitation seasonality and variability**

Jung-Eun Lee (Brown), Joseph Berry (Carnegie), Pierre Gentine (Columbia), Benjamin Lintner (Rutgers), Laura Borma (CCST/INPE), Rafael Oliveira (Campinas), Tomas Domingues (São Paulo)

### **Abstract**

The principal objective of this project is to address how vegetation influences climate variability and precipitation over Amazonian rainforests, with an emphasis on plant physiological controls on deep convection triggering along a geographical water stress gradient. To that end, we have begun development of a modeling framework using a high-resolution cloud resolving model (CRM). The CRM better simulates the seasonal and diurnal cycles of the hydrological cycle: we have found that the improvement can be attributed to the formation of a morning fog layer and variations in large-scale ascent. A morning fog layer present in the wet season but absent in the dry dramatically increases cloud albedo, and reduces evapotranspiration through its modulation of surface radiation energy budget. The temperature profile, warmer in the wet than in the dry season, mediates the seasonal transition of large-scale ascent, allowing precipitation to increase in the wet season.

Along with these CRM simulations, we have been analyzing atmospheric moisture variability from a network of GPS receivers situated in and around Manaus which provide high temporal resolution measurements of column water vapor (cwv). In particular, we have been focusing on the understanding the genesis of extremely dry conditions during the local dry season through application of FLEXPART, a Lagrangian parcel dispersion model. This is of interest given that current generation models frequently simulate too dry conditions during the Amazonian dry season.

To improve surface flux component of climate models, we have incorporated equations for SIF into a land surface model, the National Center for Atmospheric Research Community Land Model version 4 (NCAR CLM4) using existing theory and data. We demonstrate that our simulated fluorescence values are reasonable when compared with satellite (Greenhouse gases Observing SATellite; GOSAT) and *in situ* flux-tower measurements in the Netherlands. Our results overestimate GPP in tropical forests and thus indicate that maximum carboxylation rate ( $V_{max}$ ) in CLM4 may be too high in tropical forests. The model and satellite fluorescence will be compared with *in situ* measurements in the Amazon. We have been testing all of the components of fluorescence measurements in the laboratory including software. The first installation will be at the K34 tower near Manaus in summer 2015.

**Title:** Carbon cycle dynamics within Oregon's urban-suburban-forested-agricultural landscapes

B.E. Law, A. Schmidt, C. Still, T. Hilker

Our research team at Oregon State University launched a new project on the effects of land use and land cover on the exchanges of carbon, water and energy in current and future climate conditions across a gradient of urban-suburban agricultural and forested landscapes across Oregon. The region spans strong gradients from high population/high forest productivity/mesic climate in the west to low population/low productivity/arid climate in the east. Land use is changing to reduce GHG emissions.

The study is focused on the effects of (1) conversion of semi-arid sagebrush and Willamette Valley agricultural crops to bioenergy production; (2) afforestation of idle land and rangelands deemed suitable for forests or poplar crops under future climate conditions.

Policy-relevant questions are: How do current land uses and cover affect carbon dynamics, and carbon, water and energy exchanges, including cooling/warming effects? Given possible climate trajectories, what land-use strategies will reduce carbon dioxide emissions while optimizing sustainability of native vegetation and food crops?

Our approach integrates remote sensing land-use/land-cover and data from tall tower CO<sub>2</sub> observations and flux sites with comprehensive modeling approaches using the Community Land Model, CLM4.5. Artificial neural network analysis is used to examine current spatio-temporal patterns in carbon, water and energy exchange, and enhance CLM4.5 to improve its ability to predict these processes and carbon sequestration in the future.

In summer 2014, we installed flux towers in wheat and grass crops and a poplar plantation in the Willamette Valley to provide data for model parameters and testing. First results from the new flux sites indicate significant alterations in the carbon, water and energy exchange associated with land cover change in areas currently used for agriculture. For example, the wheat crop showed a change of the ratio of sensible to latent heat from 1 to 2 and 5 pre-senescence, post-senescence, and post-harvest, respectively. Annual NEP of the wheat crop is expected to be modest (e.g.  $\sim 170 \text{ g C m}^{-2} \text{ yr}^{-1}$ ; Turner et al. 2007) compared with an average of  $480 \text{ g C m}^{-2} \text{ yr}^{-1}$  (range 305-694) observed in highly productive Douglas-fir nearby (NECB and net emissions will be estimated in the future). The poplar plantation leaf-off is about 30 days prior to that of other poplar plantations in the Willamette Valley, so we will model the range of phenological transitions. Remote sensing, including phenocams, will identify timing of leaf emergence and physiological maturity and harvest in the major crop types and poplar plantations for model inputs.

We are using the new CLM4.5 model version that includes crop PFTs, and setting up the model to run at fine resolutions (4 km grid, 3-hourly). Our first analysis is to model current sources and sinks of atmospheric CO<sub>2</sub> in the western part of the region with high population/high forest productivity/high agricultural use. Then we will compare changes in modeled carbon, water and energy with conversion from the non-food crop lands to forest and/or poplar bioenergy crops under future climate conditions. Finally, we will assess the effects of land use changes expected in the whole domain, including sagebrush-steppe areas that are being converted to bioenergy crops in the semi-arid region. We will separate the future climate effects from management effects, and predict the interaction of the two.

## **Eco-hydrological consequences of drought-induced forest mortality: an observational case study in piñon -juniper woodlands in the southwestern US**

*Marcy E. Litvak, Laura Morillas-Gonzales, Greg Mauer, Dan Krofcheck*

Tree die-off events have rapidly increased across the globe in the last decade as a result of warmer temperatures and more severe droughts. In the southwestern US, where piñon-juniper (PJ) woodlands occupy 24 million ha, the turn of the century drought (1999-2002) triggered 40-95% mortality of piñon pine (*Pinus edulis*) in one of the most extensive mortality events recorded in the last century. To determine the consequences of this disturbance on the main components of the surface water balance, we conducted a girdling experiment in September 2009 where all adult piñon trees were girdled in an area of 200 m<sup>2</sup> reducing the piñon basal area of the site by 66%. We compared water fluxes measured in this girdled site (PJG) to fluxes measured simultaneously in an intact PJ woodland less than 3 km away (PJC). In addition to evapotranspiration (ET) measurements from open-path eddy covariance, canopy transpiration (ETc) was measured using sap flow probes (Granier thermal dissipation method) installed on five juniper and five piñon trees at each site. Below canopy evapotranspiration (ETbc) was derived from ET and ETc measurements. Soil volumetric water content (VWC) was monitored using TDR probes (CS610, Campbell Scientific) under the three main cover types (bare soil, under juniper and under piñon) at three depths (5, 10 and 30 cm depths) at both sites for comparison.

Total ET at the girdled site decreased slowly, but progressively, relative to the intact PJ woodland following the girdling, with annual ET 3%, 9% and 20% lower in 2010, 2011 and 2012, respectively, in the girdled site. This decrease in ET was largely due to a significant reduction in canopy transpiration following girdling (annual ETc at PJG decreased by 47%, 59% and 75% from 2010 to 2012 compared to the PJC site). Daily ET was substantially higher (44%, 14% and 18% for years 2010 to 2012) at PJG than at PJC only during the winter, especially during the very snowy winter of 2009/2010 (likely due to higher sublimation in the girdled site). Soil water content decreased following girdling, particularly under dead piñon trees (VWC<sub>0-30</sub> at PJG were on average 20%, 16% and 18% lower than at PJC for post-girdling years 2010 to 2012). In addition, surface temperatures inferred from longwave radiation measurements made at the site, and infrared canopy temperature sensors indicate that the girdled site surface temperature progressively increased from 2010-2012. Our results suggest piñon mortality leaves PJ woodlands both hotter, and drier than intact PJ woodlands. Given the extent of mortality observed in these woodlands and the predicted increase in mortality expected over the next century, these results have important surface energy balance consequences for the Southwestern US.

## Tracking the fate of Arctic carbon in a rapidly changing ecosystem

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\*Principle Investigator

Northern circumpolar soils cover 16% of the total land surface area yet account for nearly 50% of the estimated global organic carbon (C) pool. Unprecedented rates of warming and vegetation shifts (e.g. shrub expansion) may alter ecosystem C dynamics. However, our ability to predict the response of arctic C cycling is limited by significant uncertainties in our understanding of processes that may counteract or enhance SOM loss. One of our research objectives is to improve our mechanistic understanding of belowground C cycling in Arctic tundra soils. We utilize experiments with isotopically enriched (<sup>13</sup>C and <sup>15</sup>N) plant litter and enriched <sup>13</sup>C-glucose to track the fate of C and N through the soils. In a field experiment, we added isotopically enriched <sup>13</sup>C-glucose to soils dominated by two dominant arctic vegetation: *Betula nana*, a woody dwarf birch species, and *Eriophorum vaginatum*, a ubiquitous tussock-forming sedge. We hypothesized labile C additions would stimulate loss of native SOM from soils under *Betula nana* vegetation more than *Eriophorum vaginatum*. We measured <sup>13</sup>CO<sub>2</sub> efflux following C additions and are tracking the fate of this C into microbial biomass and soil C pools. We are incorporating data from these experiments into a microbe-explicit soil carbon model (MEM) to improve our ability to predict Arctic soil carbon-climate feedbacks. The MEM includes a detailed component network (soil organic C, dissolved organic C, microbes, extracellular enzymes, and mineral surfaces) to explicitly represent biotic and abiotic components and their competitive interactions. As an initial effort, we tested the model behavior using lab soil incubation data from previous publications. We will apply data from our experiments to perform model parameterization and evaluation. We will also further develop the model to be able to simulate soil C dynamics in a real Arctic soil environment. Preliminary results from our field experiments indicate greater respiration and <sup>13</sup>C-glucose utilization by soil microbes associated with *E. vaginatum* and no stimulation of native SOM loss under either vegetation type. Our <sup>13</sup>CO<sub>2</sub> efflux results suggest new inputs of labile C will not result in an immediate destabilization of native SOM. Preliminary results from our model testing and evaluations indicate that the model is able to accurately track the dynamics of each modeled soil C pool, and that microbe-mineral competitive interactions play a key role in controlling soil organic C turnover.

## Fluxes of CO<sub>2</sub>, CH<sub>4</sub>, CO, BVOCs, NO<sub>x</sub>, and O<sub>3</sub> in an Old Growth Amazonian Forest

J William Munger, Steven C. Wofsy, Kenia Wiedemann, Luciana Rizzo, Humberto Rocha, Helber C. Freitas, Julio Tota, Alex Guenther, James Smith

The Amazon Forest includes a diverse combination of vegetation characteristics, climate, and land usage that influence emission of the reactive trace-gases that influence atmospheric chemistry and particle formation. A better understanding of atmospheric chemistry across this region requires consideration of variation in precursor emissions. To complement the intensive GoAmazon measurement campaigns we have established a suite of measurements including NO<sub>x</sub>, O<sub>3</sub>, CH<sub>4</sub>, CO<sub>2</sub>, at the km67 site in the Floresta Nacional do Tapajós: 600 km east (upwind) of Manaus. The site is situated midway between the Tapajós River on the west and the BR 163 highway to the east (upwind). The nearby surroundings for up to 6 km on all sides is intact rain forest. A strip along the east side of the highway and adjacent roads has been cleared for agriculture, but the upwind area is otherwise sparsely populated. The site is away from urban sources but is influenced by the nearby agricultural activity in some seasons. Observations of CO<sub>2</sub> concentrations and flux were established at km67 in 2001. In 2014 we added a new profile inlet system to measure gradients of NO/NO<sub>2</sub>, CH<sub>4</sub>, and O<sub>3</sub> and will highlight them here. An intensive campaign near the end of wet season in June-July 2014 focused on emissions of biogenic hydrocarbons and formation of fine aerosol.

Both O<sub>3</sub> and CH<sub>4</sub> are depleted in the canopy space relative to air above the trees, demonstrating deposition to the leaves and overall soil uptake of CH<sub>4</sub> at this site. Large-scale variability in ambient CH<sub>4</sub> concentrations, however, suggest there may be some regional sources. The soils at this site appear to be strong sources of NO. NO<sub>x</sub> levels are highest close to the ground where emissions are trapped in a stagnant layer, but still approach several ppb above the canopy at night.

## Seasonal Oxygen Dynamics in a Thermokarst Bog in Interior Alaska: Implications for Rates of Methane Oxidation

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Methane is a potent greenhouse gas, and wetlands represent the largest natural source of methane to the atmosphere. However, much of the methane generated in anoxic wetlands never gets emitted to the atmosphere; up to >90% of generated methane can get oxidized to carbon dioxide. Thus, methane oxidation is an important methane sink and changes in the rate of methane oxidation can affect wetland methane emissions. Most methane is aerobically oxidized at oxic–anoxic interfaces within wetlands where rates of oxidation strongly depend on methane and oxygen concentrations. In wetlands, oxygen is often the limiting substrate. To improve understanding of belowground oxygen dynamics and its impact on methane oxidation, we deployed two planar optical oxygen sensors (40–cm wide x 60–cm deep) in a thermokarst bog in interior Alaska. Previous work at this site indicated that, similar to other sites, rates of methane oxidation decrease over the growing season. We used the sensors to track spatial and temporal patterns of oxygen concentrations over a growing season. We coupled these *in-situ* oxygen measurements with periodic oxygen injection experiments performed against the sensor to quantify belowground rates of oxygen consumption. We found that over the season, the thickness of the oxygenated water layer at the peatland surface decreased. At the start of the season (June) the oxygenated layer was, on average, 4–cm thick. By the end of the season (August) the oxygenated layer decreased to, on average, 0.5–cm thick. We also saw intermittent ~1-cm increases in the thickness of the oxygenated water layer after rainstorms. Previous research has indicated that in sphagnum-dominated peatlands, like the one studied here, rates of methane oxidation are highest at or slightly below the water table. It is in these saturated but oxygenated locations that both methane and oxygen are available. Thus, a seasonal reduction in the thickness of the oxygenated water layer could restrict methane oxidation. The decrease in thickness of oxygenated layer coincided with an increase in the rate of oxygen consumption during our oxygen injection experiments. We infer that this increase was due to a temperature enhancement of microbial reaction rates and/or an increase in substrate available for oxygen consuming reactions. Together, the data provide an explanation for the seasonal decrease in methane oxidation: rates of oxygen consumption increase over the season, which decreases the amount of oxygen dissolved in porewater at the peatland surface and reduces rates of methane oxidation.

## Methane Emissions from Upland Trees

Scott Pitz

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J. Patrick Megonigal

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Most work on methane (CH<sub>4</sub>) emissions from natural ecosystems has focused on wetlands and wetland soils because they are predictable emitters and relatively simple to quantify. Less attention has been directed toward upland ecosystems that cover far larger areas, but are assumed to be too dry to emit CH<sub>4</sub>. There is abundant evidence that upland ecosystems emit small amounts of CH<sub>4</sub> during hot moments that collectively constitute a significant source in the global budget of this potent greenhouse gas. Almost no attention has been given to trees and woody plants as significant sources of CH<sub>4</sub> in upland forests. Plant root systems integrate far larger range of soil conditions than are typically measured at the surface. Trees' roots can extend to soil depths and moistures where abundant anoxic microsites can develop. These sites can produce CH<sub>4</sub> that could enter woody plant tissue. To address these facts established a plot of upland trees in a research forest near Annapolis, Maryland. Both tree and soil CH<sub>4</sub> fluxes were measured using chamber methods with cavity ring down spectrometer. Each tree chamber was custom fit to the stem near the base. Near the plot, we also established an automated stem flux measurement system, allowing us to make high frequency measurements of fluxes at different heights and determine the drivers.

With one exception, all trees that were emitting CH<sub>4</sub> from the stems, were growing in soils that were net consumers of CH<sub>4</sub>. Upland emissions from the tree stems averaged +25 ug CH<sub>4</sub> m<sup>-2</sup> hr<sup>-1</sup> while the average soil uptake was -72 ug CH<sub>4</sub> m<sup>-2</sup> hr<sup>-1</sup>. Some stem emissions were over +200 ug CH<sub>4</sub> m<sub>2</sub> hr<sub>1</sub>. Factors controlling CH<sub>4</sub> emissions were soil moisture and Julian day.

The automated system showed fluxes followed a clear diurnal pattern and the magnitude of the fluxes decreased with height. These diurnal patterns peaked at midday and seem to be driven by transpiration. In addition, different species had similar magnitude of fluxes but the amplitude of diurnal patterns differed, indicating that species morphology may play a large role as a driver. Future CH<sub>4</sub> budgets and climate models will need to include tree fluxes and their drivers for accurate accounting and predictions.

## Effects of high-carbon regional groundwater on carbon transfers in a lowland rainforest: groundwater to surface water to air

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This project focuses on the discharge of high-carbon regional groundwater into streams and wetlands in a Costa Rican rainforest, and resultant impacts on ecosystem carbon pools and fluxes. In 2014 we measured CO<sub>2</sub> and CH<sub>4</sub> degassing fluxes from two rainforest streams at La Selva Biological Station: the Arboleda and Taconazo. In these two watersheds, only the lower Arboleda receives inputs of regional groundwater. Comparing the lower Arboleda to the upper and lower Taconazo and upper Arboleda, regional groundwater inputs: (1) increased streamwater CO<sub>2</sub> concentration by 4-6x in the dry season and 5-11x in the wet season (average increase 7x), and (2) increased CO<sub>2</sub> degassing flux by 7-15x in the dry season and 4-8x in the wet season (average increase 8.5x).

Regional groundwater input increased stream depth and lowered first-order gas exchange coefficient (time<sup>-1</sup>) in the lower Arboleda, but the two effects offset each other and there was no major effect of regional groundwater on stream gas exchange velocity.

Regional groundwater had no effect on stream methane concentration or degassing flux. Regional groundwater at La Selva is generally oxidic despite a long subsurface residence time of ~3000 yr in volcanic rock. Groundwater from regional aquifer systems of different geology may have more potential to influence stream methane, e.g., groundwater methane concentrations up to 13.3 mM (at least 100x larger than in regional groundwater at La Selva) have been found in sedimentary aquifers in Canada.

Normalized to full watershed land area, CO<sub>2</sub> degassing from the Arboleda stream was about 300 gCm<sup>-2</sup>yr<sup>-1</sup>, roughly the same as the mean NEE of CO<sub>2</sub>. Such elevated stream CO<sub>2</sub> degassing could suggest an ecosystem has elevated respiration and is a net source (rather than sink) with respect to atmospheric CO<sub>2</sub>; knowing that elevated CO<sub>2</sub> degassing is supported by large inputs of non-biogenic CO<sub>2</sub> from regional groundwater is important to not over-estimating ecosystem respiration and having a more accurate picture of the carbon source/sink status of the ecosystem.

Keeling plots were used to evaluate the signal of CO<sub>2</sub> from regional groundwater in air from stream degassing. In the Taconazo, where respiration is the only ecosystem source for CO<sub>2</sub>, δ<sup>13</sup>C-CO<sub>2</sub> vs. 1/[CO<sub>2</sub>] gave a typical straight-line Keeling plot defined by atmospheric CO<sub>2</sub> and CO<sub>2</sub> from ecosystem respiration. However, data from the lower Arboleda plotted to the upper left of this line toward higher δ<sup>13</sup>C values at higher CO<sub>2</sub> concentration, indicating the contribution of CO<sub>2</sub> from regional groundwater.

## The long and the short of it: how distinct climate drivers are affecting different components of drylands over varied timescales

Sasha C. Reed, Scott Ferrenberg, Anthony Darrouzet-Nardi, and Jayne Belnap

Like all ecosystems, drylands are made up of multiple classes of biota with varied physiologies, survival strategies, and life history traits. A factor that binds dryland organisms together is the harshness of their environment, and that the ecosystems known for high temperatures and aridity are predicted to become hotter and drier still. We will present data from a variety of timescales that show how different climate drivers (e.g., increased temperature and multiple altered precipitation treatments) affect the community composition, carbon cycling, and energy balance of drylands. Of particular interest are the results showing dramatic negative responses to altered climate – with shifts in communities and function as large or larger than those observed with physical disturbance (e.g., grazing, 4x4 vehicle use). We will discuss climate-induced changes to net CO<sub>2</sub> efflux and energy balance for both plants and soils, as well as highlight data showing the unexpected importance of under-snow carbon cycling. Finally, we will show the strong coupling between above- and belowground CO<sub>2</sub> fluxes in their response to increased temperature, but a decoupling in response to altered growing season precipitation, as well as discuss the significant variability in response among functional groups. Taken together, these data represent a significant step forward in our understanding of how different dryland organisms, biogeochemical cycles, and energy fluxes will respond to a range of future climates.

## Testing the Community Land Model (CLM 4.5) $^{13}\text{C}$ isotope simulations against high resolution observations within a subalpine forest at Niwot Ridge, Colorado

Brett Raczka, Henrique Duarte, Charles Koven, John Lin, Dan Ricciuto, Britt Stephens, Peter Thornton, David Bowling

Terrestrial biosphere models are an important tool to diagnose and predict land-atmosphere exchanges of carbon and energy. This is critical in order to quantify the land-carbon feedback into the climate system. Ecological observations are extremely important in order to quantify model skill and to improve techniques in which to simulate ecosystem behavior. Recently, carbon isotope behavior has been incorporated within CLM and we test simulated  $^{13}\text{C}$  behavior against site level observations of biomass and carbon fluxes measured at Niwot Ridge. First we 'spin-up' the model for  $\sim 2000$  years to approximate site level conditions during the 21<sup>st</sup> century. Next we use tower observed meteorology along with transient atmospheric  $\text{CO}_2$  and nitrogen deposition in order to drive the model from 1998-2013. Including the prognostic fire model within the CLM simulation provides unrealistically low biomass pools (e.g. leaf, aboveground biomass) of only 20% of the observations. The no-fire CLM simulation compares more favorably to observed present day conditions overestimating the same biomass pools on the average of 27%. The simulated seasonal cycle of the photosynthetic flux compare favorably to the flux tower observations, however the simulated ecosystem respiration is overestimated and does not capture the observed sharp increase in respiration during May. The overestimation of ecosystem respiration fluxes can likely be improved with a more accurate representation of disturbance within the simulation. During the pre-industrial period, with constant atmospheric  $\text{CO}_2$  and nitrogen deposition, CLM predicts a photosynthetic discrimination of 20 ‰ with biomass pools ranging from -26 to -26.5 ‰. This compares favorably to the site level observations. Under increasing atmospheric  $\text{CO}_2$  conditions the simulated photosynthetic discrimination increases which depletes the fast turnover pools in  $^{13}\text{C}$  first (e.g. leaf  $\delta^{13}\text{C} \sim 27$  ‰) followed by the slower turnover pools later on (e.g soil). This process leads to photosynthetic fluxes that are depleted in  $^{13}\text{C}$  as compared to the ecosystem respiration fluxes.

## Phenolic Compounds and Black Carbon Feedback Controls on Peat Decomposition and Carbon Accumulation in southern Peatlands

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Earth System Models (ESMs) predict increased frequency of extreme wet and dry periods in the subtropics and tropics over the next century, resulting in uncertain carbon (C) budgets and greenhouse gases (GHG) fluxes. Globally, approximately 1/3 of peat stores are found in subtropical and tropical peatlands (STPs) formed from high-lignin woody biomass. These peatlands have persisted through changing climate and sea level over the last 4000 years and continue to accrete peat from Virginia/North Carolina, to Florida to tropical Panama, even under climate driven conditions of drought, warmer temperatures and fire. Our main hypothesis is that the subtropical and tropical native-fire-adapted shrubs/trees communities produce higher polyphenol containing litter than northern *Sphagnum/Carex* communities. High phenolic concentrations in plant tissues prevent microbial decay of litter. In addition, low intensity fire produces black carbon and pyrogenic organic matter (PyOM) resulting in buildup of recalcitrant organic matter (OM) in the soil and leading to the formation and long-term storage of peat. Phenolic differences in conjunction with climate induced regimes of frequent low-intensity fire creates refractory decomposition-resistant peat by a dual “latch key mechanism” consisting of high phenolic and black carbon (i.e., the black carbon/PyOM complex from fire forms decay resistant aromatics). Together these retard GHG flux, and C decomposition of OM even under altered hydrologic conditions, higher temperatures and drought. Here, linking field and microcosm experiments, we show how the previously unrecognized interactions between these dual mechanisms may regulate the buildup of phenolics and black carbon/PyOM, which protect stored C directly by reducing phenolic oxidase activity during short-term drought, and indirectly through a shift from low-phenolic containing *Sphagnum/ herbs* to high-phenolic shrubs after long-term moderate drought. We also investigate whether shrub expansion caused by drought/warming in boreal peatlands might be a long-term self-adaptive mechanism not only increasing C sequestration, but also by protecting historic soil C. We therefore propose that the projected “catastrophic feedback loop” between C emissions and climatic drought and fire in peatlands is down regulated in the long-term.

## **B4WarmED: Experimental warming and rainfall manipulation in a boreal ecotone reveal key responses and adjustments at plant, soil, and ecosystem scales**

The B4WarmED experiment examines projected climate change impacts on plant and soil function at the boreal-temperate ecotone. The study includes juveniles of 11 tree species intermixed with native vegetation on 72 plots under two canopy conditions (open, understory) at two sites in northeastern Minnesota. Since 2009, plots received aboveground and belowground warming treatments (ambient, +1.7°C, +3.4°C), and since 2012 half the open plots received  $\approx 45\%$  less than ambient summer rainfall. Results provide insight into climate change impacts on boreal forest and general understanding of critical response functions that can inform earth system models.

Leaf respiration temperature response curves ( $>1,750$ ) for 10 species had remarkably consistent  $Q_{10}$  values across warming treatments, sites, canopies, and seasons. Warming treatments and seasonal variation in temperature both resulted in pronounced acclimation of leaf respiration (responses were nearly homeostatic). Acclimation was greater than reported in prior studies (done mostly in shorter time frames or less realistic conditions). The high temperature tolerance of leaves in warmed treatments was also elevated via acclimation. Across six years, phenological response to warming resulted in a longer growing season, but more so in years with early springs.

Low rainfall had more negative effects on net photosynthesis, plant growth, and survival in warmed than ambient temperatures; suggesting that lower rainfall in a warming world will have increasingly negative impacts. Species responses varied as a function of their thermal histories and water-conductance traits. Boreal species, especially conifers, were consistently more negatively affected by heat, drought, and their combination in terms of photosynthesis, growth and survival, than temperate species. Temperate angiosperms exhibited greater ability to hydraulically acclimate (with wider conduits and greater specific hydraulic conductivity) to increases in temperature than boreal conifers.

Net nitrogen mineralization measured *in situ* across 2012-2013 was significantly higher with warming, but only in open canopy treatment. Surprisingly, warming effects on net nitrogen mineralization were greatest over winter, when the warming treatment was off. From 2009-2013, *in situ* warming increased soil CO<sub>2</sub> flux, but less so in latter years. The long-term temperature sensitivity ( $Q_{10}$ ) of soil CO<sub>2</sub> flux was decreased by warming *in situ* and by drier soils in lab incubations. Impacts of treatments on ectomycorrhizae, and consequential impacts on plants and biogeochemistry, are a current major focus.

Results indicate mechanisms by which boreal species will likely perform poorly with future warming. They also provide generalized understanding and equations for better modeling of plant and soil carbon cycling processes.

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## Partitioning CO<sub>2</sub> fluxes with isotopologue measurements and modeling to understand mechanisms of forest carbon sequestration

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The interaction between forest carbon dynamics and climate is a large source of uncertainty in earth system model predictions of the future. We are investigating the mechanisms controlling carbon sequestration at the Harvard Forest by integrating stable carbon isotope analyses with a suite of measurement approaches including eddy covariance, soil chambers, plot trenching, and minirhizotrons. The data are being integrated in—and used to refine—the Ecosystem Demography 2 (ED2) model.

At the whole-ecosystem level, we used a novel 3-year timeseries (2011-2013) of <sup>13</sup>C-based isotopic partitioning of NEE into GPP and ecosystem respiration to distinguish the influences of soil water, temperature, and phenology on GPP and daytime ecosystem respiration. We consistently see large suppression (relative to nighttime) of daytime ecosystem respiration during the first half of the growing season, which we think represents the first direct detection, at the ecosystem scale, of the so-called “Kok effect” (light suppression of mitochondrial respiration in leaves, heretofore only observed by ecophysiologicalists at the leaf-scale). At the same time, we found that GPP responded consistently to light throughout the growing season, whereas conventional estimates show an anomalous peak in photosynthetic light-use efficiency early in the growing season.

At the aboveground-belowground interface, we used automated chamber measurements in trenched (i.e. no live roots) and untrenched plots to partition belowground respiration into its autotrophic (root) and heterotrophic (soil) components. The expected lower total belowground respiration in the trenched plot (due to absence of autotrophic respiration), observed in 2013, was unexpectedly reversed during a period of low precipitation in 2014. Evidently, the lack of transpiration-driven water removal in the trenched plot (detectable as wetter soil) elevated heterotrophic respiration sufficiently to compensate for the lack of autotrophic respiration. These results help us determine the separate controls on autotrophic and heterotrophic respiration.

Belowground C allocation by red oak (*Quercus rubra*), white ash (*Fraxinus americana*), and eastern hemlock (*Tsuga canadensis*) was positively correlated with temperature, though root growth occurred in multiple flushes while respiration was

unimodal. Deciduous hardwood stands allocated C belowground earlier in the season and more to root growth, relative to coniferous eastern hemlock, which allocated C later and more to exudation than root growth. These results highlight the importance of accurate modeling of C delivery to the microbial community via roots.

These observations enabled us to develop an isotope-enabled version of the Ecosystem Demography 2 model which is now being tested against the isotopic and C allocation measurements (e.g.  $^{13}\text{C}$  and  $^{18}\text{O}$  fluxes from eddy covariance and soil surface chambers). We plan to apply the eventual isotope-optimized model to data from Howland Forest (a different Northeastern forest site) to test the generality of the model's improved representation of mechanisms of C allocation and storage.

## PROCESSES CONTROLLING CARBON MINERALIZATION WITHIN PERIODIC WETLAND SOILS

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Soil contains the largest carbon stock on Earth, with approximately one-third of soil carbon stored in the tropics. An important control on soil organic matter (SOM) quantities is the mineralization (oxidation) rate, which ranges from days to millennia. The rate of SOM mineralization is affected by climatic factors influencing microbial metabolic rates in combination with SOM chemistry, mineral-SOM stabilization, and physical protection. What remains elusive is to what extent constraints on microbial metabolism induced by the respiratory pathway, and specifically the electron acceptor in respiration, control overall rates of carbon mineralization in soils. Here we sought to determine how aerobic-anaerobic cycling in soils contributes to SOM mineralization rates and thus storage.

The major factors contributing to SOM accumulation (e.g., precipitation, clay content, temperature, biological activity) are often at extremes in the tropics. We therefore used the accelerated (potential) rate of carbon processing to examine the factors controlling carbon turnover within the mega deltas of Asia, specifically focusing on the Mekong Delta, using a combination of laboratory and field experiments. We compared the abundance and chemical state of SOM at three sites having varying degrees of saturation (uncultivated seasonal wetlands, cultivated wetlands, and permanent lakes) by measuring total carbon content and chemistry, the latter deduced with bulk C (1s) near-edge x-ray absorption fine structure (NEXAFS) spectroscopy. Permanganate oxidizable carbon (POXC) measurements suggest that microbially oxidizable C is concentrated in the top 50-100 cm of the deltaic wetland soils, even when normalized to bulk C content, and that deeper SOM is minimally available for microbial oxidation.

To assess the impact of soil saturation on SOM we monitored CO<sub>2</sub> flux, porewater chemistry, and soil moisture content at a seasonal wetland through flooding and draining periods. Surface sediment cores (10 cm diameter) collected from the same wetland were manipulated in the laboratory to deduce the relative effects of drying, O<sub>2</sub> influx, and Fe mineral precipitation on observed CO<sub>2</sub> fluxes. We compared the following drying conditions: oxic, anoxic, and oxic with additional Fe(II) addition. In each of these treatments we monitored CO<sub>2</sub> flux and porewater chemistry as a function of water content during a drying cycle. After complete drying, the top 3 cm of the cores were separated into density fractions of <1.6, 1.6-2.4, and >2.4 g cm<sup>-3</sup> using sodium polytungstate solutions, and the two denser fractions were analyzed using scanning transmission x-ray microscopy (STXM). Drying under oxic conditions stimulates SOM oxidation and CO<sub>2</sub> flux relative to anoxic drying, and we observed increased mass in the <1.6 and 1.6-2.4 g cm<sup>-3</sup> fractions of the anoxic core. The formation of Fe(III) oxides during oxic drying protects SOM from mineralization as indicated by close C-Fe associations in STXM analysis. These associations are less pronounced in anoxic cores. Soils exposed to seasonal oxygen incursions accumulate less SOM than permanently flooded soils and sediments owing to oxygen-induced microbial degradation pathways; however, metal-organic matter associations provide an important preservation pathway.

## TES Program

### The impact of permafrost carbon loss on the carbon balance of an experimentally warmed tundra ecosystem

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New estimates place 1330-1580 billion tons of soil carbon in the northern circumpolar permafrost zone, more than twice as much carbon than in the atmosphere. Permafrost thaw and the microbial decomposition of previously frozen organic carbon is considered one of the most likely positive feedbacks from terrestrial ecosystems to the atmosphere in a warmer world. Understanding the magnitude, rate, and form of greenhouse gas release to the atmosphere is crucial for predicting the strength and timing of this carbon cycle feedback to a warming climate. Here we report results from seven years of an ecosystem warming manipulation—the Carbon in Permafrost Experimental Heating Research (CiPEHR) project—where we increased air and soil temperature, and degraded the surface permafrost. We used snow fences coupled with spring snow removal to increase deep soil temperatures and thaw depth (soil warming) and open top chambers to increase growing season air temperatures (air warming). The soil warming treatment has successfully warmed soils by 2-3°C in winter, has increased growing-season depth of ground thaw by up to 25-50%, and has degraded an increasing amount of surface permafrost each year of the project. The treatment has led to the development of continuously thawed soil layers deep within the profile that remain above zero even during the cold winter. We showed that experimental warming that caused permafrost degradation led to a two-fold increase in C uptake by the ecosystem during the growing season. Increased C uptake was mirrored in aboveground plant biomass changes measured by non-destructive point intercept sampling, with much of the increase due to growth of the dominant tussock-forming sedge *Eriophorum vaginatum*. Warming also enhanced growing season and winter respiration, which, in part, offset growing season C gains. This was in part due to more old carbon released by soil warming both during the growing season and the winter. Carbon exchange observations also pointed to an unexplained pattern in the air+soil warming treatment that became magnified over the course of the experiment. Each type of warming manipulation applied alone stimulated the biological processes that drive ecosystem C uptake and release. But, there was a negative interaction such that C exchange rates for the treatments together were in between the magnitudes observed for each warming treatment alone. This negative interaction was also observed in the direct measurement of aboveground plant biomass and in the patterns of soil N availability pointing towards some soil-mediated mechanism driving the interaction.

## **Determining the Drivers of Redox Sensitive Biogeochemistry in Humid Tropical Forests**

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The availability of soil oxygen ( $O_2$ ) and associated redox dynamics are key drivers of carbon and nitrogen cycling and greenhouse gas emissions in tropical forests. However, few studies have measured soil oxygen availability, and even fewer have related this to greenhouse gas fluxes over time and space. Improved mechanistic understanding of the relationship between soil  $O_2$  concentrations and greenhouse gas dynamics will improve Earth systems models. In this study, we are using field and laboratory experiments in the Luquillo Experimental Forest, Puerto Rico, to develop a mechanistically derived redox component for the Community Land Model (CLM4). We are using empirical and modeling efforts to improve the prediction of carbon, nitrogen, and phosphorous cycling and greenhouse gas dynamics in space and time. Our research tests the following hypotheses: 1) Soil  $O_2$  concentrations vary as a function of soil texture, slope position, and rainfall in humid tropical forests; 2) The spatial and temporal dynamics of soil  $O_2$  availability can be used to predict patterns in redox sensitive biogeochemical processes; and 3) Hot spots and hot moments in greenhouse gas fluxes are derived primarily from high substrate availability and secondarily from soil  $O_2$  availability.

We installed a sensor field using galvanic  $O_2$  sensors (Apogee Instruments) and time-domain reflectometry (for moisture and temperature, Campbell Scientific) along topographic gradients in a lower montane wet tropical forest in Puerto Rico. Seven sensors of each type were installed at 12 cm depth along a ridge to valley catena; the entire catena transect was replicated five times. Within the sensor field we also installed three automated gas flux chambers randomly located in each topographic zone (ridge, slope and valley). A Cavity Ring-Down Spectroscopy (CRDS) gas analyzer is being used to measure pseudo-continuous fluxes of  $CO_2$ ,  $N_2O$ , and  $CH_4$ . Our preliminary results showed that soil  $O_2$  concentrations decrease from ridges to valleys along topographic gradients. Average  $O_2$  concentrations on ridges were significantly higher than those in valleys. Moreover, soil volumetric water content in upland valleys was significantly higher than those on ridges. Both ridges and slopes produced higher  $CO_2$  fluxes than valleys ( $P < 0.05$ ). Daily  $CH_4$  emissions went up to  $\sim 2000 \text{ g } CH_4 \text{ ha}^{-1} \text{ d}^{-1}$  for valleys, which released significantly higher  $CH_4$  than ridges and slopes. Soil nitrous oxide ( $N_2O$ ) oscillated between negative and positive values across all treatments with all values mostly less than  $4 \text{ g } N_2O \text{ ha}^{-1} \text{ d}^{-1}$ . Our preliminary results suggest that soil  $O_2$  and associated redox dynamics are an important driver of gas fluxes. We also report very high  $CH_4$  emissions from valley soils suggesting that these upland soils are large net  $CH_4$  sources.

## Imparting molecular specificity to surface-modified polymeric probes for the selective capture of plant metabolites.

Metabolites released from litter leachates and root exudates help the plants to adapt to a wide range of habitats by facilitating resource foraging and by promoting plant-organismal interactions. Most of these functions are facilitated by small molecules that possess high biological activity. Hence a precise understanding of the molecular identity of these compounds is imperative to gain a mechanistic view of the processes at the plant-soil interface. Due to their high biological activity, most of these small molecules are produced and exuded at infinitesimally low concentrations. However, soils are awash with plant metabolites that are less biologically active- carbohydrates and amino acid exuded from roots, and macromolecules that are produced during the litter decomposition. Hence biologically active plant compounds are often crowded-out during the traditional analytical approaches, which hampers our understanding about the identity and dynamicity of these compounds. We previously demonstrated the application of *hyper-crosslinked* poly(styrene-co-vinylbenzyl chloride-co-divinylbenzene) probes for the *in-situ* capture of plant metabolites of low polarity from soil matrix, with a high spatial resolution. Here we further impart specificity to this copolymer matrix by using molecular-template imprinting approach for the selective capture of less abundant plant metabolites from a crowded soil/litter leachate. Specificity was imparted by developing polymeric probes through *in-situ* polymerization of matrix containing templates of plant metabolites. The specificity of these molecularly-imprinted-polymeric (MIP) matrix to capture flavonoids from soil and litter leachates were investigated. Compared to the hyper-crosslinked probes, the MIP exhibited lower surface area. However the MIP exhibited >100 times higher selectivity in retaining the proxies of the template molecules from the leachate compared to the hyper-crosslinked probes. The extraction efficiency of the adsorbed compound varied from 72-105%, resulting in detection limits of <5 ng/ml for the representative flavonoid compounds. Template leaching during sampling was addressed by using labeled molecules for imprinting. The MIP exhibited a higher LoD for glycosylated flavonoids compared to their respective aglycones. MIP were further modified to increase their aqueous-compatibility, so as to directly sample the soil solution. Utilization of MIP in conveniently usable formats will be discussed. Future work is focused on developing MIP coating on to the glass/stainless-steel rods for the *in-situ* sampling of soil solution in the field.

## Scratching the surface of belowground volatile emissions A mechanistic and VOCational analysis

TES program

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Much research has detailed the ways in which biogenic volatile organic compounds (bVOCs) present in the atmosphere influence both ecological interactions and tropospheric chemistry. However, our understanding of the sources of and controls over VOCs from terrestrial ecosystems remains incomplete, namely the relative source/sink strength of deciduous forest soils. In temperate hardwood forests, nearly all fine roots are colonized by either arbuscular mycorrhizae (AM) or ectomycorrhizae (ECM), which respond uniquely to environmental variability and have differential effects on soil organic matter decomposition with likely consequences for bVOC emissions. The primary aim of our project is to 1) quantify differences in soil bVOC uptake and/or emissions between AM and ECM dominated forest stands 2) identify the biotic, abiotic, and biogeochemical processes responsible for driving these fluxes from leaf-out to leaf senescence, and 3) consider processes occurring at or below the soil surface to potentially improve models aimed at describing atmospheric photochemistry, particularly OH reactivity.

In a temperate deciduous forest in southern Indiana, we are currently quantifying the magnitude, timing, and ecological and environmental controls of bVOC emissions from soils *in situ*. Once a month, air samples are collected from chambers established within plots containing >90% AM or ECM-associated tree species ( $n=4$ ) and analyzed using proton transfer reaction-mass spectrometry (PTR-MS). Preliminary results from the 2014 growing season show total bVOC emissions are higher in ECM forests than in AM forests. Furthermore, AM forests shift from bVOC sources to VOC sinks as the growing season progresses. However, these general patterns are not reflected for individual compounds. Together, these data suggest that variation in litter type and microbial associations between ECM and AM plots are potentially translated into differences in bVOC quality and quantity.

We will continue to measure soil bVOC emissions over time and look to correlate our findings with the environmental, biogeochemical, and biotic factors we are concurrently measuring. To tackle questions regarding sources of soil bVOCs, we have initiated a greenhouse experiment to follow the fate of stable isotopes into belowground emissions and assess associated root enzyme activity. Finally, we are using existing Ameriflux infrastructure to create a series of bVOC profiles, both within the soil and the forest canopy, in conjunction with OH reactivity measurements in order to model VOC transport through the forest and address unknown source/sink dynamics for soils themselves and their potential to affect the oxidative capacity of the troposphere.

**Scientific Focus  
Area (SFA)  
Abstracts:  
SBR Oriented**

## **The Argonne National Laboratory Subsurface Biogeochemical Research Program SFA: Fe and S Biogeochemistry in Redox Dynamic Environments**

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Understanding the interplay of the Fe and S biogeochemical cycles with the water cycle is critical for prediction of the mobility of contaminants; atmospheric greenhouse gas emissions; carbon cycling and sequestration in subsurface environments; and nutrient mobility in near-surface and subsurface polar, temperate, or tropical systems. The objective of the Argonne Subsurface Biogeochemical Research Program (SBR) Scientific Focus Area (SFA) is *to identify and understand coupled biotic-abiotic molecular- to core-scale transformations of Fe and S within redox-dynamic environments and understand the effects of Fe and S biogeochemistry on transformation and mobility of major/minor elements and contaminants*. To accomplish this objective, the Argonne SBR SFA integrates two unique strengths at Argonne — the Advanced Photon Source (APS) for synchrotron-based interrogation of systems and next-generation DNA sequencing and bioinformatics approaches for microbial community and metabolic pathway analysis — with biogeochemistry and microbial ecology. Addressing this objective contributes directly to the goal of the United States Department of Energy (DOE), Office of Biological and Environmental Research (BER), Climate and Environmental Sciences Division (CESD) to “advance fundamental understanding of coupled biogeochemical processes in complex subsurface environments to enable system-level environmental prediction and decision support” (<http://science.energy.gov/ber/research/cesd/>).

Argonne SBR SFA research addresses four critical knowledge gaps related to accomplishing this goal: (1) *an in-depth understanding of the molecular processes affecting Fe, S, and contaminant speciation in dynamic redox environments*; (2) *an understanding of the role of biogenic and abiotic redox-active products and intermediates in Fe, S, and contaminant transformations*; (3) *a mechanistic understanding of the factors controlling the mass transfer of Fe, S, and contaminants in heterogeneous media*; and (4) *an in-depth understanding of the relationship of microbial community dynamics and function and coupled biotic-abiotic controls and their effects on major/minor element cycling and contaminant transformations*.

The Argonne SBR SFA has a long-term vision of ultimately integrating the new knowledge generated by the SFA into future multiscale modeling approaches to understand and predict relevant environmental processes. The ten year vision also includes (1) an ever-increasing emphasis on integrating metagenomic-based analysis approaches for understanding community structural and functional controls on fundamental Fe and S biogeochemical processes, (2) an increasing emphasis on model development to predict the transformations and mobility of nutrients and contaminants in many subsurface and near-surface environments, and (3) expansion of these studies with a greater emphasis on using minerals and microbial communities from a network of field sites encompassing many types of redox-dynamic environments.

## Insights into Fe and S Biogeochemistry in Redox Dynamic Environments

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Biogeochemical cycling of Fe and S in the terrestrial subsurface affects contaminant mobility, nutrient availability, and groundwater chemistry. Predicting the flow of electrons through these elements requires a fundamental, molecular-level understanding of the coupled biotic and abiotic processes responsible for these transformations.

Natural Fe<sup>III</sup> oxides typically contain a range of trace elements that can include P and we examined the bioreduction of lepidocrocite and maghemite containing 0–3 mass% P. Kinetic dissolution studies showed congruent release of Fe and P, indicating that the P in these materials was incorporated within the particles. In the absence of P, lepidocrocite was rapidly and stoichiometrically reduced to magnetite by *Shewanella putrefaciens* CN32, and over time the magnetite was partially transformed to chukanovite. Doping with 0.2–0.7 mass% P significantly inhibited the initial reduction of lepidocrocite but ultimately resulted in greater Fe<sup>II</sup> production and the formation of carbonate green rust; doping with 3.0% P resulted in the formation of green rust and vivianite. However, the bioreduction of both maghemite and P-doped maghemite resulted in solid-state conversion to magnetite, with subsequent formation of chukanovite.

In separate bioreactor experiments, we show that at pH 9, dissimilatory metal-reducing bacteria (DMRB) can respire S<sup>0</sup> but not goethite because the reduction of the latter is not thermodynamically favorable under oligotrophic conditions. Because the reaction of HS<sup>-</sup> with Fe<sup>III</sup> minerals produces S<sup>0</sup>, DMRB in alkaline aquifers may require active respiration by sulfate-reducing bacteria (SRB) to respire. Under these conditions, Fe<sup>III</sup> reduction will proceed via S<sup>0</sup>-mediated electron-shuttling pathways through a mutualistic partnership between DMRB and SRB rather than the direct enzymatic reduction of Fe<sup>III</sup> minerals by DMRB alone.

Accurate determination of Fe<sup>II</sup> concentrations and distribution is key to understanding iron redox processes in environmental systems. Acid extraction followed by colorimetric assay is a widely used approach for determination of Fe<sup>II</sup> in soil and sediment samples that under sulfidogenic conditions can contain both metal sulfides and Fe<sup>III</sup> oxides. Our comparisons of Fe<sup>II</sup> concentrations determined by 0.5 N HCl extraction/colorimetric assay (ferrozine) and XAFS analysis showed that the presence of sulfide resulted in overestimation of Fe<sup>II</sup> concentrations by acid extraction by a factor of 1.5 to 3 depending on the Fe<sup>III</sup> oxide; the extent of Fe<sup>II</sup> overestimation was higher with ferrihydrite and lepidocrocite than with goethite. These results illustrate the need for caution when using acid extraction/colorimetric analysis to determine Fe<sup>II</sup> concentrations in samples containing Fe<sup>III</sup> oxides and ferrous sulfide.

## Microbial Community Structure in Redox Dynamic Environments

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Unraveling the complexity of subsurface microbial communities and their responses to dynamic environmental conditions is essential to improving our understanding of the biogeochemical cycling of major and minor elements, including contaminants. We characterized microbial communities from microcosms designed to test the effect of ethanol diffusion into U<sup>VI</sup>-contaminated sediment from the Oak Ridge IFRC. Groundwater and sediment was amended with sulfate, then ethanol was allowed to diffuse into the underlying sediment. The spatial distribution, valence, and speciation of both U and Fe were monitored *in situ* by synchrotron x-ray spectroscopy, in parallel with measurements of solution chemistry. As the ethanol was consumed concomitant with sulfate depletion, a ~1-cm layer of sediment near the sediment-water interface became visibly dark. XANES spectra in this layer were consistent with the formation of FeS and the reduction of U<sup>VI</sup> to U<sup>IV</sup>. Sequence analysis of 16S rRNA gene amplicons showed that the microbial community had evolved from its originally homogeneous composition, becoming spatially heterogeneous. At the sediment-water interface of the ethanol-amended (EtOH+) microcosms, sequences from the dissimilatory metal-reducing bacteria *Geobacter* and *Anaeromyxobacter* were by far the most abundant, accounting for 65-68% of the total community compared to 2-5% at the same location in no-ethanol controls (EtOH-). In the EtOH- samples, sulfate reducers composed 27-29% of the bacterial community, compared to only 4-7% in the EtOH+ samples. Statistical analyses showed that while ethanol was consumed within 7 days, its impact on the bacterial community was still evident after 4 years. These results indicate that even brief, one-time amendments can result in long-term perturbations of a microbial community and that these events continue to shape the community even after the resumption of static conditions.

In a separate experiment, we found that the microbial community in sediment from the Rifle IFRC was dominated by a previously-uncultivated epsilonproteobacterium, *Candidatus Sulfuricurvum* sp. RIFRC-1. Using whole-genome shotgun sequencing, we were able to reconstruct its complete 2.4-Mb-long genome *de novo* using a complexity reduction approach. Genome-based comparisons indicated that the organism is a novel species within the *Sulfuricurvum* genus. Genomic evidence suggests that RIFRC-1 is capable of growing by microaerobic or nitrate-/nitric oxide-dependent oxidation of S<sup>0</sup>, sulfide, sulfite, or H<sub>2</sub>. Consistent with these physiological attributes, the local aquifer was microoxic with small concentrations of available nitrate, small but elevated concentrations of reduced sulfur, and limited NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub>. These results provide valuable insight into the complex role of microbially-mediated sulfur cycling in the subsurface.

## Update on the factors controlling the speciation of Hg and U in laboratory reactors, flow-through columns, and natural sediments

SBR - ANL SFA (Laboratory Research Manager: Robin Graham)

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The Argonne SFA aims to provide the molecular-level information needed for the development of predictive models that inform policy decisions. The focus here is on the mechanisms of U and Hg transformations in redox dynamic environments. Our previous studies demonstrated that  $\text{Hg}^{\text{II}}$  can be reduced to  $\text{Hg}^0$  by several  $\text{Fe}^{\text{II}}$  species. Here we have tested the ability of  $\text{Mn}^{\text{II}}$  to reduce  $\text{Hg}^{\text{II}}$ . Results show that at pH 7.5, the majority of  $\text{Hg}^{\text{II}}$  is reduced to  $\text{Hg}^0$  within three hours. Reduction of  $\text{Hg}^{\text{II}}$  is coupled to the oxidation of  $\text{Mn}^{\text{II}}$  to hexagonal birnessite ( $\text{Mn}^{\text{IV}}$ ), which auto-catalyzes additional  $\text{Mn}^{\text{II}}$  oxidation. The reactivity of the birnessite phase is short-lived due to rapid evolution from the hexagonal to a triclinic polymorph, concomitant with a change to a slower rate of  $\text{Hg}^{\text{II}}$  reduction. These newly discovered mechanisms help improve Hg transport models and estimates of bioavailable Hg for methylation.

The redox transformations of U continue to be of interest due to the unknown structure and stability of the non-uraninite  $\text{U}^{\text{IV}}$  species observed in reduced sediments. We have shown that the mechanisms of  $\text{U}^{\text{VI}}$  bioreduction or the presence of trace phosphate exert significant control on the resulting  $\text{U}^{\text{IV}}$  species. We have also recently discovered that metal oxide surfaces can prevent uraninite formation and stabilize adsorbed  $\text{U}^{\text{IV}}$ . The molecular-level information accumulated on these distinct  $\text{U}^{\text{IV}}$  species is now allowing for a more precise identification of the non-uraninite  $\text{U}^{\text{IV}}$  species in contaminated sediments from the former Oak Ridge field site and of  $\text{U}^{\text{IV}}$  in naturally-reduced soils. Together with ongoing work on  $\text{U}^{\text{IV}}$  formation in the presence of clays, these results will enable an improved description of  $\text{U}^{\text{IV}}$  in transport models.

The Argonne SFA is also exploring the transformations of Fe, S, and contaminants under advective flow conditions. The initial studies here focus on comparing experimental profiles of Fe and S species in x-ray accessible columns to those predicted by reactive transport models. A column consisting of ferrihydrite-coated packing material and a sulfide-containing influent was used. The physical part of the transport model was defined by fitting the profiles of a Br tracer obtained by x-ray fluorescence measurements. The resulting dispersion coefficient was used in conjunction with a reactive network to predict Fe and S speciation along the flow path. The observed discrepancies between the measured and calculated profiles suggest the need for improvements in the reaction network based on the mechanistic information provided by the x-ray spectroscopy measurements.

**Genome-to-Watershed Predictive Understanding of Terrestrial Environments:  
Overview of the LBNL SBR SFA 2.0**

Susan S. Hubbard, Deborah Agarwal, Jillian F. Banfield, Harry R. Beller, Eoin Brodie, Phillip Long, Peter Nico, Carl Steefel, Tetsu Tokunaga, Kenneth H. Williams (all Berkeley Lab) and the SFA 2.0 Team

The LBNL ‘Genomes-to-Watershed’ SFA 2.0 project is developing predictive capabilities to quantify how the terrestrial microbiome affects biogeochemical watershed functioning, how watershed-scale processes affect the microbial community, and how these interactions co-evolve with climate and land-use changes. Development of such predictive capabilities is critical for guiding the optimal management of water resources, contaminant remediation, carbon stabilization, and agricultural sustainability – now and with global change.

Two study sites in the Colorado River Basin are serving as platforms for developing new approaches, insights and models. The Colorado River Basin is already threatened by drought, diminished snowpack, wildfires, and pest outbreaks, which have largely unexplored impacts on water, energy and other ecosystem services provided by the river corridor. Extensive characterization, field experiments, natural perturbations, and model development activities have taken place at a uranium-contaminated floodplain located near Rifle CO. Over 1,000 mostly novel subsurface genomes have been sequenced from the Site, providing some of the first insights into the diversity of the subsurface microbiome and metabolic roles of organisms involved in subsurface nitrogen, sulfur and hydrogen and carbon cycling. Metatranscriptomics have revealed the inordinate role of chemolithoautotrophy at the site. Geophysical methods have been used to document the presence of hot spots and hot moments of activity in the floodplain. Novel instrumentation has been installed to track water, carbon and nitrogen through the soil, vadose zone, capillary fringe and groundwater, providing new insights about transport across compartments and seasons. New approaches and conceptual models are being developed to quantify organic matter dynamics at mineral interfaces, and to document the mechanisms by which mineral associations affect carbon transport. GEWASC, a first-ever Genome-Enabled Watershed Simulation Capability, is being developed and tested at Rifle. Progress Trait-based and multi-scale models have been developed to represent the diversity of microbial functional processes within a larger scale reactive transport framework. Importantly, simulations have already demonstrated how incorporation of genome-informed reaction networks significantly improve prediction of terrestrial environment behavior.

Research has also been initiated at the pristine East River watershed in the headwaters of the Upper Colorado River Basin. At this site, hyporheic zone flow through organic, carbon-rich sediments located between meanders may have a large impact on carbon cycling in the river basin. Hydrological and biogeochemical measurements are being collected to quantify the fine-scale gradients, and geophysical and other measurements are being used to identify watershed larger functional zones. Models are being developed to incorporate and link the fine and large scale processes: from genomes-to-watersheds - with an eye toward extending to water basins.

## **Geophysical-based Approaches for Quantifying the Spatiotemporal Distribution of Physicochemical and Hydraulic Properties that Influence the Biogeochemical Functioning of the Rifle CO Floodplain**

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Gaining a predictive understanding of terrestrial environmental functioning requires information about the key controls on system behaviors and their variations over space and time. As part of the Genomes-to-Watershed LBNL SFA, advanced geophysical acquisition, inversion, and integration approaches are being developed to meet this objective. Here, we describe two recent advances – one associated with using geophysical and stochastic approaches to delineate the 3D distribution of hydrostratigraphic units having distinct physicochemical properties that control reactive transport, and the other focused on developing novel inversion schemes using autonomously collected, streaming datasets to jointly quantify hydraulic and thermal behaviors of the shallow floodplain subsurface. The developed characterization and monitoring strategies are being used to parameterize the genome enabled reactive transport watershed simulation capability (GEWASC) at the Rifle CO biogeochemical field study site. The approaches are also being extended based on conceptual models of hot spots and hot moments in the East River Watershed in the Upper Colorado River Basin, a developing LBNL SFA field study site.

A Bayesian approach was used with surface electrical resistivity tomography and time-domain induced polarization datasets to identify the presence and distribution of naturally reduced zones in the Rifle floodplain and their associated uncertainties. These zones are characterized by increased organic matter and reduced mineral concentrations, as well as unique microbial signatures and are considered as biogeochemical hotspots due to their importance in carbon and other nutrients cycling. The Bayesian estimation approach also took advantage of well log stratigraphy and a surface elevation model inferred from a kite-based aerial imaging platform. Results revealed that the developed approach enable a reliable mapping and uncertainty quantification of each major hydrostratigraphic units and hotspot locations.

A joint hydrogeophysical inversion framework was developed and implemented using autonomous, streaming electrical, thermal, capillary pressure and meteorological data to quantify in high resolution hydrological-thermal interactions as a function of weather conditions, snowmelt, and a variety of other forcings. Gaining an understanding of these interactions is critical due to their control in microbial mediation of key biogeochemical dynamics at the site, which have documented periodic infiltration pulses as a key hot moment controlling biogeochemical functioning of the floodplain. The developed approach used the iTOUGH2 platform, and effectively accounts for the multiphase and nonisothermal flow in porous media and for petrophysical relationships and uncertainty to link soil moisture and temperature with the electrical resistivity. Results revealed that the developed framework is adapted to quantify hydraulic and thermal parameters and understand spatiotemporal variability in water and heat fluxes. Overall, results of these efforts demonstrate the value of using various datasets collected in a minimally invasive manner and at high spatial resolution, and advanced data inversion and integration framework.

## **SEDIMENT ASSOCIATED ORGANIC MATTER DYNAMICS**

Peter S. Nico, Ruth Tinnacher, Patricia Fox, Benjamin Gilbert, Ellen Daugherty, Thomas Borch, Xiu (Joyce) Yuan, EunJu Kim, A. Cristina Cismasu

The Organic-Mineral Dynamics (OMD) component of the LBL-Genomes to Watershed SFA has the long term goal of developing and parameterizing an improved conceptual model for organic matter cycling in the subsurface that can be incorporated into the developing Genome-Enabled Watershed Simulation Capability (GEWaSC) frame work. OMD activities are focused on the saturated zone of the SFA's primary field site at Old Rifle, Co. At this location, in spite of low total organic carbon, typically ~0.1%, sediment associated OM stocks are greater than DOM stocks by approximately three orders of magnitude. This disproportionate stock of sediment associated OM strongly supports the hypothesis that interactions between organic matter and mineral surfaces are a key regulator of OM transport and transformation. Accordingly, the research activities under OMD focus on elucidating the mechanisms that control OM-mineral interactions with a particular focus on sorption/desorption and co-precipitation processes. These processes are explored in the context of fluctuating redox conditions and changing DOM concentrations and characteristics. Efforts to characterize and quantify the types of sediment associated organic matter are presented in more detail in a companion poster by P. Fox et al, entitled 'Characterization of Natural Organic Matter (NOM) in Low Organic Carbon Environments: Approaches and Implications for Reactivity.' This poster in turn will focus on the other activities that constitute the OMD component of the LBL SFA. Results presented in this poster will include 1) characterization of the Fe-OM co-precipitates formation during a simulated oxidation event and the subsequent aging and re-organization of those materials; 2) release into solution and fractionation of sediment associated OM when exposed to OM free synthetic ground water; 3) thermodynamic analysis of metal binding by organic matter and organic matter association with mineral surfaces; and 4) the mechanism of organic matter binding of Fe(II), 5) the kinetics and mechanism of model organic matter compound oxidation catalyzed by Fe redox cycling.

## Characterization of Natural Organic Matter in Low Organic Carbon Environments: Approaches and Implications for Reactivity

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Sediment-associated natural organic matter (NOM) is an extremely complex assemblage of organic molecules with a wide range of sizes, functional groups, and structures, which is intricately associated with mineral particles. The chemical nature of NOM may control its' reactivity towards metals, minerals, enzymes, and bacteria. Organic carbon concentrations in subsurface sediments are typically much lower than in surface soils, posing a distinct challenge for characterization. As a part of the Genomes to Watershed LBNL SFA 2.0 we investigated NOM associated with shallow alluvial aquifer sediments in a floodplain of the Colorado River in Rifle, Colorado, USA. Total organic carbon (TOC) contents in these subsurface sediments are typically around 0.1%, but can range from 0.03% up to approximately 1.5%. Total organic carbon content is largely correlated with sediment texture, which is highly heterogenous in this aquifer, with the highest TOC contents associated with naturally-reducing zones. Even at the typical TOC values of 0.1%, the mass of sediment-associated OC is approximately 5000 times higher than the mass of dissolved OC, representing a large pool of carbon that may potentially be mobilized or degraded under changing environmental conditions. The goals of this study were to characterize the sediment-associated NOM and determine the degree to which it varies across different biogeochemical regimes present within the Rifle aquifer.

We have characterized the sediment-bound NOM from two locations within the floodplain with differing physical and geochemical properties. One location has relatively low organic carbon (<0.2%) and is considered suboxic [dissolved oxygen is low or absent, but no dissolved Fe(II) observed], while the other is a naturally reducing zone (NRZ) with higher organic carbon (0.2-1.5%) and Fe(II)-reducing conditions. A NOM extraction scheme was developed using a combination of sequential extraction [water and sodium pyrophosphate (pH 10)] and purification (dialysis and solid phase extraction) in order to isolate different fractions of sediment-associated NOM. Analysis of these different NOM fractions was then carried out by FTIR and ESI-FTICR-MS to allow for comparison of NOM structure and composition both across sites and across fractions for a single location. Using this combination of analytical techniques we can probe the variation in NOM chemical composition and mineral association across different biogeochemical regimes and assess the potential reactivity of various NOM pools. In combination with targeted field and laboratory experiments, this information can be used to determine key NOM characteristics to consider in modeling the biodegradation, transformation, and flux of carbon under changing conditions.

## Isotopic Insights into Nitrogen Cycling in the Rifle Subsurface

*LBNL SBR SFA (Laboratory Research Manager: Susan Hubbard)*

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Nitrogen is a key nutrient supporting microbial activity in the subsurface sediments. The biological availability of nitrogen is dependent on several important processes including nitrogen fixation (conversion of atmospheric N<sub>2</sub> to ammonia), nitrification (conversion of ammonia to nitrate) and denitrification (anaerobic reduction of nitrate to N<sub>2</sub>). Other processes include assimilation by microbes, oxidation of various intermediates and anammox (anaerobic oxidation of ammonia and nitrite to N<sub>2</sub>). Isotopic measurements of the different reactants, intermediary compounds and products are very useful for distinguishing the occurrences of these different processes in nature. As part of the LBNL SFA at the Rifle site in western Colorado, we have been monitoring the concentrations and isotopic compositions of N<sub>2</sub>O, an important intermediary in several of the processes listed above, in soil gas samples collected from the unsaturated zone. In addition, measurements of the concentrations and isotopic compositions of nitrate in pore water from the same wells have also been done. These samples were collected from suction lysimeters installed in the Rifle vadose zone with sampling ports at 0.5 m intervals down to the groundwater table. During the late spring/early summer, snowmelt causes the level of water in the adjacent Colorado River and groundwater to increase by as much as 2 m, inundating the lower sampling ports. During and just after this high-water episode, the concentrations of N<sub>2</sub>O in soil gas from the deeper intervals increase to as high as 39 ppmv (versus normal background concentrations of ~5-10 ppmv). Coinciding with these sharp increases in N<sub>2</sub>O is a decrease in pore water nitrate concentrations from >5mM to <1mM in the deeper sampling ports.  $\delta^{15}\text{N}$  values of the nitrate increased from a background composition of approximately 2‰ to as high as 13‰ during the groundwater level rise before slowly recovering to background compositions. Conversely, the  $\delta^{15}\text{N}$  of the N<sub>2</sub>O decreased from background compositions averaging about -5‰ to as low as -16‰ before slowly increasing to background. Despite the changes in the difference between the nitrogen isotopic compositions of the N<sub>2</sub>O and nitrate ( $\Delta^{15}\text{N}_{\text{Nitrate-N}_2\text{O}} = 10\text{‰}$  in the winter and ~30‰ following the rise in the water table), the isotopic compositions are consistent with denitrification being the primary source of the N<sub>2</sub>O. The changes in the concentrations and nitrogen isotopic compositions of the nitrate and N<sub>2</sub>O suggest that slow build up of pore water nitrate occurs during fall through early spring with low levels of denitrification to N<sub>2</sub>O and subsequent denitrification of the N<sub>2</sub>O to N<sub>2</sub>. During the water level rise and shortly thereafter, flooding of the lower vadose zone rapidly depletes the pore water nitrate, producing a pulse of low  $\delta^{15}\text{N}$  N<sub>2</sub>O.

## Metatranscriptomic evidence of diverse chemolithoautotrophy in the Rifle (CO) subsurface relevant to C, S, N, and Fe cycling

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The Genomes-to-Watershed Scientific Focus Area (SFA) 2.0 aims to develop a predictive understanding of how climate or land-use induced changes can affect overall watershed biogeochemical functioning. At the Rifle (CO) study site, this scope includes influx of dissolved oxygen or nitrate into a perennially suboxic/anoxic aquifer containing a large reservoir of reduced Fe- and S-containing compounds. The role of the "Metabolic Potential" component of SFA 2.0 is to characterize prevalent metabolic pathways in subsurface microbes and to use these data to inform the next generation of trait-based microbial models (GEWaSC).

Although there is only a limited understanding of the chemolithoautotrophic activity of aquifer microorganisms, such subsurface microbial activity could greatly influence the cycling of elements such as C, S, N, and Fe. Here, we present transcriptional (RNA-Seq) evidence of the occurrence of such chemolithoautotrophic activities in groundwater filter samples from a 2-month experiment in which up to 1.5 mM nitrate (a native electron acceptor) was injected into the Rifle aquifer. Illumina sequence data from rRNA-subtracted cDNA libraries was mapped to metagenome-derived genomes.

Metatranscriptomic analysis revealed pervasive and diverse chemolithoautotrophic bacterial activity in the Rifle subsurface. More specifically, chemolithoautotrophic bacteria with very high-ranking genes in the metatranscriptomes of at least some samples included the following: (1) member(s) of the Fe(II)-oxidizing Gallionellaceae family, (2) anammox bacteria, i.e., planctomycetes capable of anaerobic ammonia oxidation, (3) the S- and Fe(II)-oxidizing *Thiobacillus denitrificans* and (4) member(s) of the facultatively anaerobic S-oxidizing *Sulfuricurvum* genus. High-abundance transcripts belonging to these bacteria had very high sequence identity to known representatives (e.g., a cold-shock protein with 98% sequence identity to that in *Gallionella capsiferriformans*; a hydrazine oxidoreductase gene with 93% identity to that of the anammox planctomycete KSU-1; and an APS reductase with 99% identity to that of a *T. denitrificans* strain that we isolated from the Rifle aquifer). These four groups of chemolithoautotrophs had different temporal patterns of expression throughout the experiment. Surprisingly, anammox transcripts maximized in the pre-release sample (even though nitrite, the electron acceptor for anammox, is not detectable in native groundwater) and Gallionellaceae transcript abundance correlated very strongly with nitrate consumption (even though reported isolates are microaerophiles). A reconstructed Rifle *Gallionella* genome encodes the nitrate reductase *napA* and associated genes, suggesting an explanation for the strong correlation of Gallionellaceae transcripts with nitrate. These data provide key insights into the important role of chemolithoautotrophy in the Rifle subsurface and are being used to inform modeling efforts.

## Genome-resolved metagenomics provides a comprehensive view of microbial metabolism in the subsurface

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Microorganisms drive transformations of carbon compounds in the terrestrial subsurface, an important reservoir of carbon on earth, and impact many other linked biogeochemical cycles. Despite this, little is known about the identity and metabolic capabilities of the vast majority of microbes in the subsurface. This lack of understanding of the microbial processes that impact carbon turnover in the subsurface has restricted the ability of climate models to capture key aspects of the carbon cycle. Here, we used a genome-resolved approach to decipher the metabolic capabilities and roles of the uncultivated microbial majority in the subsurface. We sequenced groundwater and sediment microbial communities sampled from four different geochemical environments from an aquifer adjacent to the Colorado River, near Rifle, CO, USA. Reconstruction of genomes followed by manual curation resulted in the recovery of 2,542 high-quality genomes, 18 of which are complete. Phylogenetic analyses involving 16S ribosomal RNA genes and other ribosomal proteins revealed that less than 11% of these genomes belonged to the 4 most commonly represented phyla in public databases, that constitute 93% of all currently available genomes. A large proportion of the genomes we recovered belong to phyla that were previously unknown or lacking cultured representatives. Genome-specific analyses of metabolic potential revealed the co-occurrence of important traits involving electron donors (e.g. organic carbon, sulfur, hydrogen, methane, ammonia), electron acceptors (e.g. oxygen, nitrate, sulfate), carbon fixation, and nitrogen fixation. Coupled analyses of genomic abundance and metabolic potential provide unprecedented information on microbial functional redundancy and heterogeneity across time (~6 years) and geochemical environments (sediments, groundwater). Our study significantly advances the understanding of the genetic underpinnings of microbial diversity and function in the subsurface. These predictions of microbial metabolic potential will serve as inputs into LBNL's Genome-Enabled Watershed Simulation Capability (GEWaSC) modeling effort.

## GEWaSC Modeling of the Rifle Floodplain Aquifer: Hydrological, Biogeochemical, and Microbial Controls on Carbon, Nitrogen, and Oxygen Fluxes

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The Genome Enabled Watershed Simulation Capability (GEWaSC) is being used to address the principal controls on carbon, nitrogen, and oxygen fluxes in the surface and subsurface portions of the Rifle floodplain. Previous studies have identified naturally reduced zones (NRZs) in the saturated alluvium associated with elevated organic carbon, Fe(II), sulfide, and U(IV). These reduced areas are important drivers of biogeochemical fluxes from the dominantly sub-oxic floodplain into the Colorado River. The seasonal rise and fall of the Rifle floodplain water table, as well as the seasonal variation in surface temperatures, creates transient conditions in which leaching and mixing of reactive vadose components into the groundwater exert an important control on biogeochemical conditions and reaction rates in the subsurface aquifer.

2-D and 3-D variably saturated flow and reactive transport models have been developed to address multiple terminal electron acceptor processes (TEAPs), kinetic and equilibrium mineral precipitation and dissolution, as well as spatially distinct pools of Fe and S minerals and functional microbial populations. New proteomics-informed metabolisms include nitrate-dependent Fe(II) oxidation, oxygen-dependent Fe(II) oxidation, fermentation of DOM, nitrate reduction and microaerophilic heterotrophy. Microbial contributions from chemo(litho)autotrophic processes (e.g., ammonia, sulfur and iron oxidation) appear to be prominent.

2-D model simulations, in which NRZs were self-organized from initially homogeneous conditions, focused on abiotic and biotic contributions to CO<sub>2</sub> fluxes along a well-instrumented transect. The dynamics of these fluxes were consistent with observed seasonal water table variations, temperature fluctuations, and isotopic systematics in the vadose zone. The modeling indicated that the observed CO<sub>2</sub> fluxes cannot be explained by abiotic reactions alone, but required contributions from chemo(litho)autotrophic microbial activity. In particular, <sup>13</sup>C profiles in the vadose zone points to a microbial rather than abiotic origin for the elevated CO<sub>2</sub> concentrations in the NRZ.

3-D floodplain modeling, incorporating geophysically-delineated NRZs, focused on the impact of NRZs and local vadose zone conditions on redox cycling involving Fe, O, S, N, and C. The descending water table limb brings O<sub>2</sub> and nitrate to depth, leading to the oxidation of FeS, which liberates Fe(II) and sulfate into solution. Arrivals in the groundwater of U(VI), Ca<sup>2+</sup>, sulfate, and Sr<sup>2+</sup> prior to the water table peak are associated with vadose zone remnants of mill tailings that were not replaced with fill material.

Both 2-D and 3-D simulations will eventually incorporate kinetic parameters derived from trait-based models, also developed under GEWaSC, which is expected to significantly reduce the limitations of current simulations.

## Genomes to Watershed LBNL SFA 2.0: Modeling Microbial Community Dynamics with Genome-Informed Trait-Based Models

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The Genomes to Watershed SFA 2.0 is focused on addressing uncertainties in how climate or land-use-induced changes in hydrology and vegetation will affect subsurface carbon flux, the spatial and temporal distribution of flow and transport, biogeochemical cycling, and microbial metabolic activity. Here we report on the development of a Genome-Enabled Watershed Simulation Capability (GEWaSC), which provides a predictive framework for understanding how genomic information in a subsurface microbiome affects biogeochemical watershed functioning, how watershed-scale processes affect microbial function, and how these interactions co-evolve. In recent years, cultivation-independent approaches have further elucidated knowledge of microbial functional diversity within the subsurface. With the emerging capability to reconstruct thousands of genomes from microbial populations using metagenomic techniques and gene expression data, there is a need to develop an understanding of how these metabolic blueprints influence the fitness of organisms and how populations emerge and impact the physical and chemical properties of their environment.

We have developed a hybrid trait-based reaction transport model of microbial activity (BioCrunch) that simulates coupled guilds of microorganisms. Guild selection is driven by traits and physiological properties extracted from large-scale assembly of metagenome data. Metagenome information is also used to complement our existing biogeochemical reaction networks and contributes key reactions where biogeochemical analyses are equivocal. Our approach models the rate of nutrient uptake and the thermodynamics of coupled electron donors and acceptors for a range of microbial metabolisms including heterotrophs and chemolithoautotrophs. Exogenous substrates fuel catabolic and anabolic processes, with the proportion of energy used for each based upon dynamic intracellular and environmental conditions. In addition to biomass development, anabolism includes the production of key enzymes, such as nitrogenase for nitrogen fixation or exo-enzymes for the hydrolysis of extracellular polymers. This internal resource partitioning represents a trade-off against biomass formation and results in microbial population emergence across a fitness landscape. We use this model in simulations of biogeochemistry within the Rifle floodplain system, a component of the greater Colorado River system. Simulations and metagenomic/metatranscriptomic observations identify a number of functional guilds with chemolithoautotrophic lifestyles that appear to be important in mediating elemental cycling within aquifer biogeochemical hotspots. In addition, key processes regulating aquifer oxygen concentrations during seasonally fluctuating water table regimes are explored.

## **Genomes to Watershed Data Management and Assimilation**

A software infrastructure and platform is being developed for data management and assimilation [DMA] as part of the LBNL Genomes to Watershed SFA 2.0, with components and capabilities driven by the project science priorities. The overall objective of the DMA software platform and infrastructure is to enable the users to integrate and synthesize diverse and disparate field, laboratory, and simulation datasets, including geological, geochemical, geophysical, microbiological, hydrological, and meteorological data across a range of spatial and temporal scales. The current focus of the DMA effort is to (a) develop an integrated interface to the data (brokering and portal system), (b) store field monitoring data, laboratory analytical results of water and sediments samples, and metadata collected at the Rifle, Colorado, field site into a database, and (c) provide basic automated QA/QC analysis of stored data and work with data providers to modify field and laboratory data collection and reporting procedures as needed.

We have developed, tested and released a first version of our broker system that integrates diverse datasets from the RifleDB and ggkBase. This data includes hydrological parameters (water level and water temperature), geochemical analyses and metagenomic data. We have deployed a beta version of the user interface portal for the broker, based on an extensive user-centered design process. This initial version focuses on helping users find the data needed to complete analyses through an intuitive interface. Once the data is found, the user can immediately plot and download data through the portal. The interface is based on an interactive visualization, created using D3.js.

The RifleDB continues to be our primary database for storage of non-metagenomic data collected at the Rifle site and we continue to expand and improve the database. We implemented and validated automated QA/QC analyses of high-temporal resolution water level data collected by 29 pressure transducers in monitoring wells at the Rifle site. We also implemented a QA/QC analyses for vadose zone and groundwater temperature and geochemical data collected in monitoring wells, as well as meteorological data. We have provided recommendations related to the standardization of the field water-level measurements, water sampling, and reporting of the results of field and laboratory measurements.

The future goals of the DMA team include further development and testing of the brokering system, ingestion of the field and laboratory data to enable reliable integration and synthesis of diverse and disparate field, laboratory, and simulation datasets across different spatial, and temporal scales.

From Rifle to RMBL: MODEX activities at LBNL's new RMBL/East River field site

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As part of LBNL's Genomes-to-Watershed Scientific Focus Area (SFA) research program, Modeling-Experiment (MODEX) activities have begun at a new field station within the upper East River catchment, located near the town of Crested Butte, Colorado. The East River is one of two major tributaries that form the Gunnison River, which in turn accounts for just under half of the Colorado River's discharge at the Colorado/Utah border. Emblematic of many mountain headwater catchments within the upper Colorado River Basin, the site is home to the Rocky Mountain Biological Laboratory (RMBL), which enables data sharing related to hydrology, meteorology, phenology, and coupled vegetation-microbiology studies of direct relevance to LBNL's SFA program.

Data collection activities started in May 2014 indicate the site is well suited for addressing the primary research objective of the LBNL SFA project, which is to quantify the impact of climate-induced changes in hydrology and vegetation on biogeochemical functioning at the scale of the watershed. Initial observations suggest varying responses in water isotope composition and nutrient concentration to changes in river discharge. Hyporheic exchange between the East River and its associated floodplain deposits has been shown to induce sharp gradients in redox sensitive elements, with gaining reaches exhibiting evidence of carbon mineralization coupled to a variety of reductive pathways. Pools of sediment-associated carbon exhibit strong spatial gradients in both total concentration and lability.

The catchment is presently being modeled at 10m resolution using ParFlow, a parallel, integrated hydrologic model. Driven by meteorological forcing, ParFlow is able to capture land surface processes and represents surface and subsurface interactions through saturated and variably saturated heterogeneous flow. The model assesses hydrologic changes accompanying shifts in both meteorological inputs and vegetation distribution to capture variations in energy and water budget components. In the near term, coupling this watershed model with one describing a diverse suite of genome-resolved elemental cycling pathways, including carbon, nitrogen, and sulfur transformations, will provide an improved understanding of the response of the subsurface biome to hydrologic transitions induced as a result of global climate change. In addition, a low gradient subdomain within the larger catchment model serves as one of two use cases for DOE's IDEAS project. The East River use case seeks a better understanding of aquifer redox status and climate impacts on watershed carbon and nitrogen cycling through higher fidelity, multi-scale models simulated at high spatial resolution.

**Scientific Focus  
Area (SFA)  
Abstracts:  
TES Oriented**

## Environmental Transport of Plutonium: Biogeochemical Processes at Femtomolar Concentrations and Nanometer Scales

SBR

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A major scientific challenge in environmental sciences is to identify the dominant processes controlling actinide transport in the environment. This is particularly difficult for the light actinides (Pu and Np in this work) due to their complex redox chemistry. Unexpected observations of kilometer scale Pu transport have raised concerns regarding our understanding of the fundamental biogeochemical processes controlling Pu transport. As a result, the mission of LLNL's SFA has been to:

*Identify the dominant biogeochemical processes and the underlying mechanisms that control actinide transport (focusing on Pu and Np) in an effort to reliably predict and control the cycling and mobility of actinides in the subsurface.*

To date, our research has focused on the following five processes:

1. Sorption-desorption and surface mediated redox processes on mineral surfaces,
2. Complexation with organic matter and formation of ternary mineral-ligand-actinide complexes,
3. Pu-oxide precipitation in the presence and absence of mineral surfaces
4. co-precipitation and mineral phase alteration, and
5. direct and indirect microbial interactions.

Highlighted below are recent results (FY14) for each of the five processes investigated above:

- Identified Pu(IV/V) sorption linearity and quantified surface-mediated Pu(V) reductions rates on goethite, montmorillonite, and bentonite over an eight order of magnitude range in Pu concentration ( $10^{-7}$  to  $10^{-15}$  M).\*\*
- Began quantifying Pu sorption/desorption kinetics on goethite, montmorillonite and bentonite to assess field scale colloid-facilitated transport mechanisms (including surface mediated redox transformations).

- Identified the potential role of hydrogen peroxide at environmental concentrations in oxidizing and mobilizing Pu(IV).
- Evaluated the formation of aqueous Pu-NOM and ternary Pu-NOM-mineral complexes for fulvic acid, humic acid, and DFOB in the presence of gibbsite, goethite, and montmorillonite,\*\*
- Developed actinide NMR capabilities at LLNL to probe Np(VI) ligand exchange kinetics and identify the structure of Pu-DFOB complexes responsible for irreversible intercalation into montmorillonite.
- Determined the structure and stability of Pu nanoparticles on goethite as a function of time (3 months) and temperature (25°C and 80°C), and
- Characterized the behavior Pu(V/IV) on bound-EPS and EPS-free cell surfaces of *Pseudomonas* sp. strain EPS-1.\*\*

\*\*Three additional posters discuss our results in further detail.

New knowledge gained from this SFA is advancing our understanding of the behavior of actinides, providing DOE with the scientific basis for remediation and long-term stewardship of DOE's legacy sites and, more broadly, increasing our understanding of actinide behavior in environmental systems.

## Plutonium Sorption to Mineral Surfaces at Attomolar to Micromolar Concentrations

SBR

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A focus of the LLNL SFA has been the study of Plutonium (Pu) sorption and desorption in simple binary systems at concentrations ranging from those commonly observed in the field ( $<10^{-12}$  M) to higher concentrations that are routinely used in laboratory experiments ( $10^{-6}$  to  $10^{10}$  M). This experimental effort has addressed concerns that sorption behavior determined at concentrations used in laboratory measurements might not be representative of sorption processes occurring under actual subsurface conditions.

We have investigated the sorption behavior of Pu(V) and Pu(IV) over a minimum of 8 orders of magnitude in Pu concentration ( $10^{-8}$ – $10^{-15}$  M) onto Fe-oxyhydroxide (goethite), clay mineral (montmorillonite) and clay rock (bentonite) at pH 8. In addition, we investigated Np(V) sorption to goethite over an initial concentration range of  $10^{-5}$ – $10^{-18}$  M. Pu(V) sorption was found to be broadly linear over a range of initial concentrations from  $10^{-6}$ – $10^{-16}$  M for montmorillonite and  $10^{-6}$ – $10^{-15}$  M for goethite. Similarly, Pu(IV) sorption to goethite also appeared linear over an initial concentration range of  $10^{-5}$ – $10^{-15}$  M. In contrast to the Pu isotherms, Np(V) sorption to goethite exhibited a non-linearity that implies the presence of high-affinity sorption sites. However, the nature of these high-affinity sites has yet to be determined.

The sorption of Pu(IV) and Pu(V) to goethite reached equivalent sorption equilibria within 15 days. In contrast, the sorption of Pu(IV) to montmorillonite was greater than Pu(V) after 30 days. After 1 year, the Pu(V) isotherm matched the Pu(IV) data, indicating that equilibrium was achieved but only after 3 months. We attribute the slow sorption to continued reduction of Pu(V) to Pu(IV) on the mineral surface and stress the need to account for such slow processes when predicting field-scale transport.

Importantly, our experimental data accumulated in the past three years as part of this SFA indicate that the affinity of Pu for mineral surfaces will not increase significantly at ultralow Pu concentrations compared to higher concentrations routinely used in the laboratory ( $10^{-9}$ – $10^{-11}$  M). However, above  $10^{-9}$  M, Pu(IV) can precipitate as an intrinsic oxide. The results have broad implications to our conceptual understanding of processes controlling colloid facilitated Pu transport and, more broadly, to contaminant reactive transport. Pu sorption processes and associated kinetics identified at moderately high concentrations ( $<10^{-9}$  M) appear to be scalable to ultra-low femtomolar environmental concentrations, justifying the use of existing experimental data in transport models.

## Stabilization of Pu Surface Complexes on Mineral Colloids by Natural Organic Matter

SBR

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The LLNL SFA has been examining the influence of natural organic matter (NOM) on Pu sorption to minerals. The major objectives have been to determine the affinity of Pu for NOM, identify the conditions that lead to the formation of ternary Pu-NOM-mineral complexes, and quantify the stability and mobility of those complexes.

We determined thermodynamic data for Pu-NOM complexes by determining stability constants for Th(IV)-, Np(V)-, and Pu(IV)-HA (humic acid) complexes using a discrete pKa approach. Comparison of Th(IV)-HA and Pu(IV)-HA complexes to others actinide-ligand complexes revealed a consistent pattern in which Pu(IV) complexes are nearly four orders of magnitude more stable than their Th(IV) counterparts.

Pu sorption to montmorillonite, gibbsite and goethite in the presence of desferrioxamine B (DFOB), HA, fulvic acid (FA), HA and citric acid (CA) was examined. When compared to the binary Pu-mineral systems, the addition of CA, FA, HA decreased the sorption of Pu(IV) at circumneutral pHs. A similar effect was observed with the addition of DFOB to gibbsite and goethite. In contrast, when Pu(IV) was equilibrated with DFOB prior to addition of montmorillonite, a significant increase in Pu(IV) sorption was observed. However, when DFOB was equilibrated with montmorillonite prior to addition of Pu(IV), Pu(IV) sorption was equivalent to the binary system. X-ray diffraction and TEM revealed that DFOB accumulated in the interlayer of montmorillonite. The irreversible nature of DFOB accumulation in the montmorillonite interlayer leads to an apparent dependence of Pu sorption on the order of addition. The results highlight the importance of siderophores/hydroxamate ligands as Pu complexants and the unique intercalation mechanism that can lead to irreversible Pu sorption to layered clays.

The effect of NOM on Pu adsorption/desorption kinetics was also investigated. In goethite suspensions at low pHs, we found that FA coatings slowed Pu adsorption kinetics, while aqueous FA accelerated Pu surface reactions. Independent of the initial form of FA, FA increased Pu sorption in low-pH environments and stabilized Pu on the mineral surface above a solid concentration of  $\sim 0.20$  mg TOC  $g_{\text{goethite}}^{-1}$ . Furthermore, the presence of FA led to surface complexes on the goethite surface that appeared to be less reversible than the simple binary complexes. Thus FA and other NOM may increase Pu colloid facilitated transport by 1) enhancing the Pu sorption to colloids and 2) enhancing the stability and mobility of the colloids. Alternatively, NOM could decrease Pu mobility through enhanced retention on a host rock.

## Direct and Indirect Microbial Interactions with Pu and Colloids

SBR

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Microorganisms are associated with a variety of radioactive materials at DOE sites and it is becoming known that they can influence Pu speciation and solubility. However, few attempts have been made to identify the microbial populations existing at Pu contaminated DOE sites. In addition, there is a general lack of knowledge concerning the impact that microbial direct mechanisms (e.g., diversity, reduction capacity) or indirect mechanisms (e.g., exopolymer production potential) have on the subsurface mobility of Pu. These knowledge gaps limit progress on understanding the role of microbes affecting the environmental transport of Pu. *Pseudomonas sp* strain EPS-1 was isolated from Nevada National Security Site (NNSS, formerly Nevada Test Site), cultured, and its EPS extracted and purified. The interaction of Pu with *Pseudomonas sp.* strain EPS-1 and the EPS isolated from this strain was investigated to identify the role of EPS in Pu-microbe interactions and redox transformations.

EPS, a major organizational element of microbial biofilms, provides an overall protective structural stability to the microbial community. Cell-bound EPS, serving as the outermost layer of the cell surface, is likely to play a major role in cell interaction with Pu. Pu(V) complexation studies using bound-EPS isolated from *Pseudomonas sp.* strain EPS-1 confirmed that EPS rapidly reduces Pu(V) to Pu(IV). Identification of EPS component responsible for this reduction is under investigation.

To determine the redox behavior of Pu in the presence of whole cells, a series of Pu-sorption experiments was carried out with *Pseudomonas sp.* strain EPS-1 at pH 6.8 using both Pu(IV) and Pu(V). Pu concentrations were held at  $10^{-10}$  M (below solubility) and the concentration of *Pseudomonas* cells varied between  $10^8$  and  $10^6$  cells/mL. In the Pu(IV) experiments, Pu sorbed to both cells containing bound-EPS and cells that had their bound-EPS removed. At cell concentrations of  $10^8$  cell/mL, approximately 75% of the Pu(IV) attached to the surface of cells regardless of the presence of EPS. In the Pu(V) experiments, over 80% of Pu sorbed to cells containing bound-EPS while only 22% of Pu sorbed to cells that had their bound-EPS removed. The relatively low percentage of Pu(V) sorbed to the cells without bound-EPS suggests that EPS drives the reduction of Pu(V) to Pu(IV) and the subsequent association of Pu(IV) with the cells. TEM imaging of Pu(IV) and Pu(V) associated with *Pseudomonas sp.* strain EPS-1 indicates that the initial oxidation state of Pu will lead to morphologically distinct Pu-EPS associations.

## **Biogeochemical and Molecular Mechanisms Controlling Contaminant Transformation in the Environment**

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Anthropogenic releases and changing environmental conditions lead to profound impact on the biogeochemical cycle of trace metals, such as mercury (Hg). Mercury can be methylated to form methylmercury (MeHg), which bioaccumulates in the food web, endangering humans and other biota. Since its inception 6 years ago, the Oak Ridge National Laboratory (ORNL) Science Focus Area (SFA) program has made substantial progress in fulfilling the original overarching objective of ***elucidating the mechanisms by which inorganic mercury (Hg) is transformed into MeHg at the sediment–water interface and the processes that determine net MeHg production at contaminated sites***. The program's progress has resulted in a number of groundbreaking insights and discoveries, including the discovery of the Hg methylation genes (*hgcAB*) and their organismal and environmental distribution, the dual functional role of DOM in Hg redox transformation, and the fact that certain anaerobic microorganisms are capable of using dissolved elemental Hg(0) for methylation.

Our efforts since the last review have led to the realization that exchange and feedback processes occurring at critical interfaces are key factors limiting our predictive understanding of net MeHg production in environmental systems. Critical interfaces connect different ecosystem compartments and subsystem components enabling exchange, feedback, and co-evolution. In the spring, this SFA will undergo DOE peer-review. The Renewal Proposal aims to generate new knowledge in three thrusts: microbial community dynamics; fundamental biogeochemical processes; and molecular scale interactions that control Hg speciation, bioavailability, and transformations at critical interfaces along the hydrologic transport pathway. Accomplishing these objectives will contribute to the SFA's 3-year goal of ***determining the fundamental mechanisms and environmental factors that control Hg biogeochemical transformations at critical interfaces in terrestrial and aquatic ecosystems***.

This system science program integrates hydrology, geochemistry, microbiology, and computational science, including molecular simulations, to investigate Hg behavior in environmental systems. The multidisciplinary and multiinstitutional program is supported by ORNL's core expertise in field-to-laboratory scale geochemistry and microbiology and its world-class neutron source and high-performance computing capabilities. Newly generated tools and knowledge will enable a deeper understanding of Hg and trace metal speciation and flux across critical interfaces, improving predictions of trace metal biogeochemical cycles in heterogeneous and multiscaled environmental systems locally and globally.

## **Mechanisms and factors controlling photochemical transformation of mercury and net methylmercury formation in the aquatic environment**

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Atmospheric deposition of mercury (Hg) is the main source for methylmercury (MeHg) formation and bioaccumulation in fish in natural aquatic environments. Under natural sunlight, the net MeHg formation in water is strongly influenced by photochemical transformation of Hg and MeHg, in which Hg photoreduction, photooxidation, and MeHg photodegradation can occur simultaneously. However, the underlying mechanisms and factors that control these processes are not completely understood, especially the role of naturally dissolved organic matter (DOM) in freshwaters. It is also unclear whether the photo-redox transformation of Hg or Hg-DOM complexes may alter Hg reactivity and thus its bioavailability for microbial uptake and methylation. In this study, we show that Hg(II) photoreduction and Hg(0) photooxidation proceed concurrently in a Hg contaminated stream system—East Fork Poplar Creek (EFPC) in Oak Ridge, Tennessee. Carbonate ( $\text{CO}_3^{\cdot-}$ ) radicals primarily drive the Hg(0) photooxidation in EFPC. DOM and various organic ligands is found to increase MeHg photodegradation, but the first-order rate constants vary greatly depending on the oxidation state of DOM, and the type and concentrations of the complexing ligands, and the irradiation wavelength. Compounds containing both thiol and aromatic moieties within the same molecule (e.g., thiosalicylate and reduced DOM) increased MeHg photodegradation far greater than those containing only aromatics or thiols (e.g., salicylate or glutathione, or their combinations). The thiols and aromatics in DOM synergistically enhanced MeHg photodegradation. Importantly we also found that light exposure of Hg(II)-DOM solutions decreases MeHg production by *Geobacter sulfurreducens* PCA, particularly under the ultraviolet (UV) light. The decreased methylation upon light exposure coincided with decreased Hg(II) reactivity, measured by stannous-reducible Hg(II), and the UV is more effective than solar light in decreasing the reactivity. Collectively these studies identify previously unrecognized pathways for Hg(0) photooxidation, MeHg photodegradation, and the loss of Hg(II) reactivity and bioavailability upon light exposure. These findings are important to assess and predict Hg geochemical cycles and the net MeHg formation and bioaccumulation in natural aquatic environments.

## **Periphyton biofilms generate methylmercury in a contaminated creek system**

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The results of previous SFA research on mercury methylation in East Fork Poplar Creek (EFPC) in Tennessee imply key controls on net methylation occur within the stream or on the stream bed. The large diel variability in dissolved methyl mercury (MeHg) concentration appears to be correlated with the daily photocycle and the sparse wetlands (< 3% watershed area) are poorly connected to the main channel of the creek. Methylmercury is generated in fine-grained channel margin deposits along the creek but the extent of these deposits, coupled with the rates of Hg methylation, suggest these locations account for only a portion of the MeHg in the water. This phase of our research is designed to elucidate the role of periphyton biofilms in MeHg production in the creek. Periphyton is ubiquitous throughout the creek and redox gradients created within them can support Hg-methylating microbial activity. Periphyton growth surfaces deployed at upstream (closer to the historic point source of contamination) and downstream locations (~17 km apart) are collected following ~8 weeks colonization in the creek. These samples are subsequently used in laboratory assays of inorganic Hg methylation and MeHg demethylation. Enriched stable isotopes of Hg are employed to distinguish new activity from ambient background levels during incubations. Subsamples for microbial community analysis and *hgcAB* gene abundance are also collected. Redox gradients within the periphyton samples are quantified using voltammetric microelectrodes. Results to date demonstrate that both mercury methylation and MeHg demethylation occur within the periphyton biofilms. Both processes are adequately described by pseudo-first-order kinetic expressions. Clear differences in methylation and demethylation activity exist between the upstream and downstream sites and across seasons. Both methylation and demethylation potentials are higher at the downstream site. Pseudo-first-order rate constants are ~100× lower with a 10°C decrease in temperature. Although both methylation and demethylation occur in the periphyton, the rate of methylation is greater than the rate of MeHg demethylation suggesting periphyton is a net source of MeHg to the creek.

## Complex organic ligands affecting mercury uptake and methylation

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Toxic methylmercury (MeHg) is produced by certain anaerobic bacteria, and recent study has shown that two genes, i.e., *hgcA* and *hgcB*, are required for the methylation process. However, methylation is an intracellular reaction, requiring the uptake and transport of mercury (Hg) across the outer and inner membranes of the bacteria. Cell uptake and transport depend on the Hg speciation, the nature of ligands present in the surrounding media, and the characteristics of proteins on cell surfaces. Studies have shown that the presence of cysteine (Cys) enhances the uptake and methylation of Hg by *Geobacter sulfurreducens* PCA, but not by *Desulfovibrio desulfuricans* ND132, and the underlying mechanism and actual role of cysteine on Hg uptake are still not fully understood. Questions remain with regard to whether (i) cysteine is exchanging Hg(II) with the ligands/proteins on cell surface, (ii) Hg-Cys complexes interact with the cell surface through specific binding, or (iii) Hg-Cys complexes directly enter into the cells. Here we systematically investigate the effects of cysteine and selected bis-thiol chelator ligands, such as 2,3-dimercaptopropanol and dipeptides (Arg-Cys), on Hg uptake and methylation. We report that cysteine competes with cells for Hg binding and decreases Hg sorption and methylation initially in a phosphate buffered saline solution but, for unknown mechanisms, over time the *G. sulfurreducens* PCA cells were able to overcome the initial competition for Hg, leading to uptake and enhanced methylation, even at a high cysteine concentration (1000  $\mu\text{M}$ ). The amount of methylated Hg appeared to correspond well with the neutral Hg-complexes (i.e.,  $\text{HgCl}_2$  and  $\text{Hg}(\text{Cys})_2\text{H}_2$ ) in solution, while both MeHg and the neutral complexes were at lowest levels in the presence of  $\sim 0.1$   $\mu\text{M}$  cysteine. Our results also show that bis-thiol chelators and Arg-Cys peptide strongly inhibit Hg(II) uptake and methylation as compared to control experiments. These results indicate that the effect of cysteine and complexing organic ligands on Hg(II) uptake and methylation is highly complex, and additional research is needed to elucidate the roles of cysteine and natural organic ligands in the Hg methylation process.

## **Toward Understanding the Biomolecular Mechanism of HgcA**

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Our team combines experimental and computational approaches to understand the molecular-scale biophysical processes involved in mercury (Hg) transformations in the environment. Previously, we identified a two-gene cluster required for mercury methylation in anaerobic bacteria. The genes encode a corrinoid protein, HgcA, and a ferredoxin, HgcB, consistent with roles as a methyl carrier and electron donor, respectively. A strictly conserved Cys residue in HgcA was predicted to be a ligand to Co(III) in the corrinoid cofactor and to play a key role in methyl transfer to Hg substrates. More recently, the importance of this residue has been confirmed through in vivo Hg methylation experiments. Our current focus is on characterizing HgcA and elucidating its biochemical mechanism. The effects of Cys coordination on the redox properties of the corrinoid cofactor in HgcA are not well understood. Here, we have used density functional theory (DFT) to compute standard reduction potentials of a selection of corrinoids. Our calculations are in good agreement with experimentally measured values, and reveals new insight into the redox properties of the HgcA. This work will contribute to elucidating the mechanism of Hg methylation involving the HgcAB system in anaerobic microorganisms.

## Reconstitution and spectroscopic characterization of the corrinoid protein HgcA

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Subsurface Biogeochemical Research Program: ORNL Mercury SFA (PI: E.M. Pierce)

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Mercury methylation is an enzyme-catalyzed process associated with the metabolic activity of anaerobic bacteria and archaea. It has been shown that a two-gene cluster is required for mercury methylation in *Desulfovibrio desulfuricans* ND132 and *Geobacter sulfurreducens* PCA. The genes encode a cobalamin-dependent protein, HgcA, and a 2[4Fe-4S] ferredoxin, HgcB, consistent with roles as a methyl carrier and electron donor required for cofactor reduction, respectively. Among bacteria and archaea with sequenced genomes, gene orthologs are present in all confirmed methylators but are absent in nonmethylators, suggesting a mercury methylation pathway common to all methylating bacteria and archaea.

The current focus of our studies is on the cobalamin binding domain of HgcA (HgcA-CBD), as it may participate in catalyzing the transfer of a methyl group to a Hg(II) species. HgcA-CBD was expressed heterologously in *E. coli* as a maltose-binding protein fusion to enhance solubility. After purification by ion-exchange chromatography and gel filtration under strictly anaerobic conditions, we characterized the binding of cobalamin to HgcA-CBD using UV-Vis spectroscopy. HgcA-CBD binds one equivalent of cobalamin *in vitro* with a typical cofactor occupancy of >90%. The reconstituted protein was characterized by cyclic voltammetry and UV-Vis spectroscopy to investigate redox potentials and redox states relevant for activity. The spectroscopic data are consistent with coordination of a Cys thiolate to the cobalt center of the cofactor in HgcA. Cyclic voltammetry indicates that the midpoint potential for the Co(II)/Co(I) couple is close to -560 mV (vs NHE). The present results suggest that, in addition to a methyl donor, a continuous source of low-potential electrons is required for continued activity of HgcA *in vivo*. To determine the structure of HgcA-CBD at atomic resolution by NMR spectroscopy in collaboration with EMSL, we have collected preliminary data of isotopically labeled (<sup>13</sup>C, <sup>15</sup>N) HgcA-CBD. Complemented by structural bioinformatics and computational studies, the spectroscopic and structural characterization of HgcA will provide unprecedented insights into the biochemical mechanism and metabolic role of HgcA in Hg-methylating bacteria and archaea.

## **Development of Molecular Tools for the Accurate Assessment of Mercury Methylation Potentials in any Environment**

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Mercury methylation produces the neurotoxic, highly bioaccumulative methylmercury (MeHg) and requires two proteins (HgcA and HgcB). Gene detection and quantitation to determine at risk environments is critical. Universal degenerate PCR primers spanning *hgcAB* were developed to capture the organismal gene diversity in all Hg-methylators from the *Deltaproteobacteria*, *Firmicutes* and methanogenic *Archaea*. Hg-methylator quantitation was addressed by developing degenerate qPCR primers for *hgcA* for each Hg-methylating clade. To validate primer specificity, pure cultures (including methylators and non-methylators: 12 *Deltaproteobacteria*, 7 *Firmicutes*, and 6 methanogenic *Archaea*) were assayed. A single agarose gel band was observed for the majority of these organisms with known *hgcA*, validating this approach. Additionally, each clade-specific qPCR primer set only amplified *hgcA* within its clade. To mimic an environmental sample, gDNA from all clades is being combined in different ratios to assess qPCR primer specificity.

In the ecological context, we sought to combine *hgcA* abundance and diversity with MeHg generation rates and site geochemistry. We performed 16S rRNA and metagenomic sequencing on eight Hg-contaminated sites ranging from tidal marshes to Arctic permafrost. Custom algorithms were used to filter *hgcAB* from the metagenomes. For all sites, geochemical parameters (Fe, SO<sub>4</sub>, S<sup>2-</sup>) as well as Hg(II) and MeHg were quantified. In the metagenomes, the *Deltaproteobacteria* dominated the *hgcAB* pool from all sites while *Firmicutes* and *Archaea* were each 50% less abundant. In parallel, *hgcAB* clone libraries were constructed for each site. The clone library approach allowed us to verify the identity of *hgcAB*+ organisms by mapping sequences back to the 16S data. Comparison of the qPCR with the metagenomes determined the accuracy of the qPCR primers. Development of degenerate qRT-PCR *hgcA* primers is underway. The development and validation of these highly specific and quantitative molecular tools will allow for the rapid and accurate risk management assessment in any environment.

Globally, we queried *hgcAB* diversity and distribution in all available microbial metagenomes. The genes were found in nearly all anaerobic, but not in aerobic, environments including the open ocean. Critically, *hgcAB* was absent in ~1500 human microbiomes, suggesting a low risk of endogenous MeHg production. New potential methylation habitats included invertebrate guts, thawing permafrost, coastal “dead zones”, soils, sediments, and extreme environments, suggesting multiple routes for MeHg entry into food webs. Several new taxonomic groups potentially capable of Hg-methylation emerged, including lineages having no cultured representatives. Here we are generating a new global view of Hg-methylation potential.

## **Pacific Northwest National Laboratory SFA: Hydro-Biogeochemical Process Dynamics in the Groundwater-Surface Water Interaction Zone**

PNNL SFA (Laboratory Research Manager: Charlette Geffen)

John Zachara\*<sup>1</sup> (PI; [john.zachara@pnnl.gov](mailto:john.zachara@pnnl.gov)), Jim Fredrickson<sup>1</sup> (Co-PI), Tim Scheibe<sup>1</sup> (Co-PI), Xingyuan Chen<sup>1</sup>, Glenn Hammond<sup>2</sup>, Maoyi Huang<sup>1</sup>, Chongxuan Liu<sup>1</sup>, Chris Murray<sup>1</sup>, Hyun-Seob Song<sup>1</sup>, and James Stegen<sup>1</sup>

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The PNNL SFA is developing a predictive understanding of the groundwater-surface water interaction zone (termed the subsurface interaction zone, SIZ). Research explores linkages with the water cycle and incorporates hydrologic impacts on fundamental biogeochemical and ecological processes into a multiscale modeling framework that forecasts system responses and feedbacks to environmental changes. The SIZ is a ubiquitous and biogeochemically active domain at the groundwater-surface water interface that regulates contaminant releases to surface waters and associated carbon and nitrogen cycling. A key aspect of our research is the performance of observational, experimental, and computational science on contaminant, carbon, and nitrogen transformation dynamics in the SIZ within the context of an integrative multiscale modeling approach. This approach will enable bi-directional (up- and down-scale) transfer of knowledge, process models, and parameters to the desired scale of prediction. Using the 75 km Hanford Reach of the Columbia River as our overall field site, overarching research questions are driven down from the reach scale to focus lower-scale scientific hypotheses on essential system attributes, behaviors, or mechanisms for robust process model development. A facies-based, multiscale simulation framework is being established to connect biogeochemical transport models across scales while preserving robust process descriptions derived at local field sites along the Hanford Reach and with field derived sediments in the laboratory. New microbial ecological models are being formulated and tested to translate microbial community composition and function into biogeochemical process rates dependent on environmental conditions. Our research on the subsurface interaction zone will provide essential knowledge and relevant models for rivers worldwide that flow through glacio-fluvial aquifers and for high latitude/elevation catchments with coarse-grained sediments that are vulnerable to climate change.

## CLM-Agni-Akuna Integration Demonstration: A Community Platform for Uncertainty Quantification

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The U.S. Department of Energy (DOE) office of Environmental Management (EM) is investing in development of a numerical modeling toolset called ASCEM (Advanced Simulation Capability for Environmental Management) to support modeling analyses at legacy waste sites. ASCEM is an open source and modular computing framework for predicting contaminant fate and transport in natural and engineered systems. The ASCEM toolset includes a data management and user interface platform (called Akuna) integrated with a simulation controller (called Agni), which work together to develop and execute simulations of subsurface flow and reactive transport using a high-performance computing multi-process simulator (called Amanzi). The Akuna-Agni platform provides the user interface and toolsets for managing workflows, including model development starting with definition of the conceptual model, management of data and metadata for model input, sensitivity analysis, model calibration and uncertainty analysis, model execution on diverse computational platforms, and processing of model output, including visualization.

Development of the ASCEM toolset has incorporated scientific advances developed by the Subsurface Biogeochemical Research (SBR) program, and SBR program managers and investigators have been actively involved in the ASCEM project since its inception. ASCEM components have been developed using advanced software development methodologies, with an emphasis on modularity, portability and extensibility to maximize utility by a broad user community. Although the ASCEM project is focused on the Amanzi subsurface reactive transport simulator, the Akuna-Agni platform can be customized to link to other simulation tools, facilitating reuse of system components such as data management, visualization, uncertainty quantification, sensitivity analyses, and parameter estimation that are useful to a wide range of earth systems modeling efforts.

This poster describes a collaborative demonstration project undertaken by members of the PNNL and LBNL SBR Scientific Focus Area projects and other key collaborators at those two institutions. We have customized the Akuna-Agni platform to integrate the Community Land Model (CLM) simulator, and are applying this system to several research sites to demonstrate its capabilities. Completed demonstrations include 1) 1D CLM simulations of the NGEE-Arctic site, with sensitivity analysis performed on several soil parameters (e.g., organic content, percent clay and sand), and 2) 1D CLM simulations of the ARM Southern Great Plains (SGP) site, with sensitivity analysis of ten parameters (with results compared to a previous publication using a different method) and application of the parameter estimation toolset. We are also working toward demonstrations of 3D CLM simulations at the NGEE-Arctic and Hanford 300 Area sites.

## Development of Genome-Informed Reaction Network and Dynamic Models for Simulating Biogeochemical Processes of Carbon, Nitrogen, Chromium and Technetium in Subsurface Systems

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Biogeochemical reaction network and dynamic metabolic models are being formulated and tested for simulating microbial community functions and the biogeochemical transformation of carbon, nitrogen, chromium, and technetium in the subsurface interaction zone – SIZ (zone of groundwater-surface water mixing). Biotic and abiotic experiments, functional gene and enzyme assays, and multi-scale kinetic analysis are being performed to characterize kinetic biogeochemical reactions controlling the transformation of organic carbon, nitrate, and contaminants (Cr and Tc); and the production of gaseous species ( $\text{CO}_2$  and  $\text{N}_2\text{O}$ ) in SIZ sediments from two Hanford Reach locations. The transformation of nitrate and nitrite to gaseous  $\text{N}_2\text{O}$  and  $\text{N}_2$  coupled with organic carbon oxidation to  $\text{CO}_2$  was observed to correlate with dynamic changes in functional genes and enzymes regulating the denitrification processes. The resulting robust data set provides both a model simulation target and a well-defined reaction system for rigorously evaluating genome-informed metabolic models. This evaluation will proceed over the next year using two different model conceptualizations of microbial community functions responsible for denitrification: cybernetic control and system-level entropy production. In our first experiments with newly collected Hanford Reach hyporheic zone sediments, we have observed that Cr(VI) is reduced rapidly to sparingly soluble Cr(III), implying that SIZ sediments have significant reduction capacity that may limit Cr and Tc discharges from groundwater to surface water. In similar experiments, a multi-rate model has been developed to account for the effects of heterogeneous redox-reactive mineral phase distributions and fine-scale facies variations on the macroscopic rate of Tc(VII) reduction to Tc(IV). Collectively these results form the basis for an integrated multi-component kinetic reaction network model for describing the biogeochemical transformations of organic carbon, nitrate, and contaminants in the SIZ and up-scaled domains of the Hanford Reach.

This presentation is part of SBR/PNNL\_SFA.

## **Coupled Microbial-Biogeochemical Responses to Groundwater-Surface Water Mixing**

James Stegen, Evan Arntzen, Xingyuan Chen, Jim Fredrickson, Glenn Hammond, Chris Murray, Bill Nelson, Dave Kennedy, Eric Roden, Mike Wilkins, and John Zachara

The zone of groundwater-surface water mixing—the subsurface interaction zone (SIZ)—is an important component to the functioning of integrated surface/subsurface ecosystems. Due to the mixing of complementary electron donors and acceptors, the SIZ is a biogeochemical hotspot with significant influence over material transformation, the cycling of C and N, and the fate of contaminants. Relatively little is known, however, about the microbial communities that drive biogeochemical reactions in the SIZ. This is a broad knowledge gap that must be filled to link microbial ecology with hydro-biogeochemical models. To better understand SIZ microbial communities and their responses to changing biogeochemical conditions we used the Hanford site 300 Area as a model system to perform field investigations in the near-shore hyporheic zone (~ 1m below the Columbia River) and across the broader SIZ (~50-100m from the Columbia River shoreline). Hyporheic microbial communities showed elevated biomass and aerobic respiration rates in times of groundwater-surface water mixing, but this was not true of microbial communities in the broader SIZ. The collective results imply that mixing introduces labile carbon to the hyporheic, but organic carbon introduced to the broader SIZ is more recalcitrant. A sharp decline in dissolved oxygen during mixing in the hyporheic zone, but not in the broader SIZ, further supports this inference. A preliminary laboratory experiment suggested that river water itself is not the labile carbon source, leading to the hypothesis that labile carbon is transported into the hyporheic zone from riverbed sediments. Application of ecological theory to the dynamics of microbial community composition revealed that a unique selective environment emerges during times of mixing in the hyporheic zone and that microbial community dynamics in groundwater or surface water are relatively stochastic. Microbial taxa that showed significant shifts in relative abundance during mixing were associated with the ability to oxidize a broad range of organic compounds. This suggests that a generalist strategy—in terms of electron donor usage—is selected for during mixing in the hyporheic zone. These results are currently being integrated with hydro-biogeochemical modeling with the aim of improving predictions of SIZ biogeochemical function as hydrodynamics respond to variations in the hydrologic cycle. Field investigations are also being extended to couple microbial ecology to identified sediment facies to enable spatial predictions of microbial community properties relevant to SIZ biogeochemical function.

## **Facies-based mapping of hydro-biogeochemical attributes to subsurface and surface water interaction zone at the Hanford site**

Jason Hou, Chris Murray, Tim Scheibe, Evan Arntzen, Rob Mackley, Tim Johnson, Xingyuan Chen, and John Zachara

**Abstract:** A facies conceptualization can be employed in a complex multiscale hydro-biogeochemical (HBGC) modeling system as a vehicle for reducing system complexity and analyzing inter-scale relationships. In this study, we aimed to identify hydrogeological facies at the Hanford Reach for both river bed (i.e., recent alluvium) and older subsurface strata (i.e., Hanford and Ringold formations, both inland and beneath the recent alluvium), develop reliable relationships linking facies to HBGC attributes, and eventually assign HBGC properties to the modeling domain in terms of multiple field realizations at multiple scales as required inputs for multiscale modeling and uncertainty quantification of subsurface-surface water interaction processes. For the river facies definition, the Folk-Wentworth classification and hybrid hierarchical clustering approaches were applied to particle size data from freeze-core sediment samples collected from several campaigns. The lithofacies developed from the particle size data are then compared to the river bathymetry data and thermal imagery data with a much larger extent and spatial coverage, for extension of the facies definition to larger scales covering areas with few sediment samples. Supplementary constraints for the river facies definition are derived from geophysical measurements and geologic mapping along the river bank. For example, surface-based 3D time-lapse electrical resistivity tomography (ERT) helps identify the preferential flow paths and illuminate the shape of the lower confining unit of the aquifer; while induced polarization measurements are being used to map mud layer thickness along the river bed (see poster by Johnson et al.). HBGC properties are then mapped using geostatistical methods to the river bed layer by sampling from the property distributions for each facies using options such as locally varying mean. Subsurface facies are being defined separately for the high-permeability Hanford and low-permeability Ringold formations, using existing particle size data. The Hanford–Ringold contact, a key hydrologic feature, is being mapped stochastically, and will be extended beneath the river. The transition probability indicator simulation method will be used to map lithofacies in the subsurface modeling domain. HBGC properties will then be mapped to the lithofacies using geostatistical methods. The approach for development of an integrated lithofacies model of the river bed and older subsurface strata over multiple scales will initially be developed in the 300 Area, where relatively dense data can be used to test the stratigraphic and lithofacies models. The approach will then be extended to the larger domain of the Hanford Reach following refinement and optimization.

## **Hydrogeophysical Data Assimilation for Characterizing Aquifer Heterogeneity at a Groundwater and River Water Interface**

*PNNL SBR SFA (Principal Investigator: John Zachara)*

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Dynamic exchange between groundwater and river water is the dominant force that controls hydrological and biogeochemical processes at their interface. Accurate characterization of heterogeneous aquifer permeability at this interface is critical for understanding and modeling coupled hydro-biogeochemical processes that occur within their interaction zone. The distinct contrast in specific conductivity (e.g., dissolved salts) between river water and groundwater allows application of a cost-effective technology called time-lapse electrical resistivity tomography (ERT, see poster by Johnson et al.). ERT can provide indirect spatial-temporal data for characterizing aquifer permeability by imaging the change in subsurface electrical conductivity driven by mixing between groundwater and river water. We installed a 300 m by 300 m three-dimensional ERT array to monitor the temporal dynamics of river water intrusion and retreat along a major river corridor. The resulting four-dimensional electrical geophysical data was assimilated to invert for the underlying permeability field using ensemble-based algorithms (e.g., ensemble Kalman filter and ensemble smoother).

A new high-performance multi-process code was developed by coupling a flow and transport code (PFLOTRAN) with an ERT imaging code (E4D). The coupled code provides key modeling attributes of multi-physics processes, parallel efficiency, and multi-realization simulation capability for data assimilation. We sequentially assimilated both well-based point measurements of water table elevation and specific conductance, and spatially/temporally continuous ERT images with ensemble-based data assimilation techniques. Our study demonstrates the effectiveness of joint hydrogeophysical data assimilation for characterizing hydrologic properties in the groundwater and river water interaction zone. The integration of multi-scale and multi-type data with a complex multi-physics model through Bayesian data assimilation techniques, and the use of high performance computing to meet the intense computational demand was a significant scientific achievement. The resulting permeability field provides essential insights on the hydraulic controls on river water intrusion and the locations of biogeochemical hotspots where nutrients from groundwater and surface water converge.

## **SLAC SFA: Coupled cycling of organic matter, uranium, and biogeochemical critical elements in subsurface systems**

**Program Affiliation:** Subsurface Biogeochemical Research

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Natural organic matter (NOM) profoundly affects the behavior of redox-active contaminants and biogeochemical critical elements (*BCEs*, including C, N, S, and Fe) in subsurface systems where NOM is abundant. Many thin, discontinuous bodies of reduced organic-rich sediments have been observed in the uranium-contaminated floodplain at the Rifle, CO DOE research site. These naturally reduced zones have elevated U(IV) concentrations (*ca* 100-fold higher than uranium in surrounding sediments) along with abundant iron sulfides and other redox-active metals. The potential susceptibility of these zones to oxidation raises the concern that U(IV) stored in reduced sediments may be slowly oxidized and released back to groundwater, thus contributing to the ongoing plume-persistence problem at this site. We have recently observed uranium- and sulfide-enriched zones at other uranium-contaminated former ore processing sites, including Grand Junction and Naturita, CO, and Riverton WY, suggesting that organic-rich zones have the potential to mediate uranium mobility at plume persistence sites generally within and peripheral to the upper Colorado River Basin (CRB).

The SLAC SFA is investigating natural organic matter (NOM)-uranium interactions across a range of scales, from molecular to regional, to understand the fundamental biogeochemical properties and processes that govern biogeochemical response of organic-rich reduced zones. Questions being investigated include: (i) What controls the speciation of U(IV) in these zones?; (ii) What/how do microbial interactions control redox transition pathways for uranium, NOM, and BCEs in these biogeochemically complex systems?; (iii) How do organic ligands influence uranium reduction?; (iv) What processes control uranium release from reduced sediments?; (v) What are the physical and biogeochemical characteristics of organic-rich reduced zones?; and (vi) How do organic-rich reduced zones interact with surrounding floodplain aquifers?

We are using an integrated suite of approaches to address these questions, including field-scale investigations at sites across the upper CRB coupled to laboratory investigations of organic-rich sediment properties and reactivity; molecular microbial ecology; stable isotope techniques, spectroscopic and electrochemical studies of the molecular speciation and thermodynamics of uranium, NOM, and BCEs; combined x-ray, electron, and isotope microscopy imaging, and biogeochemical modeling. By collecting and integrating information across a range of scales, we will improve our understanding of these systems at all scales and locations. These activities are leading to new process-level paradigms to quantitatively describe the reactivity of organic-rich zones and their potential to impact uranium mobility, and are helping to advance SRB modeling competencies at floodplain and regional scales.

## SLAC SFA: Biogeochemistry of U(IV) and carbon in organic-rich sediments in the upper Colorado River Basin

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Fine-grained, organic-rich sediments are common in the uranium-contaminated floodplain at the Rifle, Colorado DOE research site. Many of these sediment zones are reduced and exhibit U(IV) concentrations up to 100-fold higher than uranium in surrounding sediments, along with abundant iron sulfides and other redox-active metals. Exposure of naturally reduced zones (NRZs) to oxidizing conditions has the potential to re-release stored U(IV), which has prompted us to better understand their physical and biogeochemical characteristics. NRZs are believed to be general features of floodplains, leading to the hypothesis that they are regionally important in contaminated alluvial aquifers within the upper Colorado River Basin (CRB). The SLAC SFA is studying: (i) U(IV) biogeochemistry in contaminated upper CRB floodplains and (ii) the reactivity and composition of organic carbon (OC) within NRZs. By collecting and integrating information at the regional scale, we are improving our understanding of the reactivity of NRZs and their potential to impact uranium mobility and biogeochemical critical element (*BCE*, including C, N, S, and Fe) cycling.

In the past year, we have investigated NRZs at Grand Junction, Gunnison, Naturita, and Rifle, CO; Riverton, WY; and Shiprock, NM. As part of this effort, we performed induced polarization (IP) geophysical measurements to delineate subsurface regions enriched in (semi)conductive mineral phases, such as metal sulfides, often present within NRZs. IP data collected across the Rifle floodplain were used to define drilling locations where NRZs subsequently were recovered. IP surveys conducted at the Shiprock and Gunnison sites have identified potential subsurface distributions of NRZs, which will be sampled in spring and fall 2015.

New sediment cores from the Grand Junction, Naturita, Rifle, and Riverton sites show that NRZs are indeed present at these locations. Both U and sulfide were found to be concentrated in NRZs, supporting our initial hypothesis. C K-edge X-ray absorption spectroscopy (XAS) shows that bulk organic carbon (OC) in NRZs exhibits the same functional group types and relative abundances as the OC in surrounding organic-poor sediments, possibly indicating that OC in both locations has the same source. XAS and Fourier transform-ion cyclotron resonance-mass spectrometry (FT-ICR-MS) are being used to discern differences in OC speciation in NRZs and neighboring organic-poor sediments through examination of the following fractions: water extractable C, particulate C, micro-aggregate associated C (metal-complexing, freshly precipitated mineral fraction), and mineral-associated C. Overall these results are helping to

shape new models for biogeochemical cycling of uranium and BCEs in organic-rich aquifer sediments.

## SLAC SFA: Molecular mechanisms controlling U(IV) release from organic-rich sediments: role of nitrification and denitrification

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Elevated uranium concentrations exist in fine-grained, organic-rich sediments (ORS) in contaminated floodplains at ore processing sites across the upper Colorado River Basin. Recent evidence from Rifle, CO suggests that microbial nitrogen cycling is stimulated by seasonal groundwater table fluctuations. Nitrate and nitrite produced by this activity are strong oxidants for U(IV). Consequently, there is concern that biogeochemical nitrogen cycling drives re-release of uranium from ORS to groundwater. The SLAC-SFA is investigating this subject using an integrated program of (i) laboratory incubation and column studies of Rifle sediments, (ii) studies of functional gene markers for nitrifying and denitrifying organisms, and (iii) biogeochemical reactive transport modeling.

Rifle ORS were exposed to nitrate in diffusion-limited reactors. The greatest amount of aqueous U(VI) was released during the first two weeks of the experiment; however, solid-phase associated U(VI) continued to accumulate within 1 cm of the sediment-solution interface until the end of the experiment (70 days). Our work suggests that U(IV) oxidation by nitrate occurs on a time scale relevant to the field (ca. 2 – 3 months), but that release of aqueous U(VI) is diffusion-limited once the U(IV) at the sediment-solution interface is depleted. Experiments underway are investigating whether water-level fluctuations can promote nitrification of ammonium present in the sediments, causing seasonally elevated nitrate concentrations.

We are also investigating the diversity and abundances of nitrifying and denitrifying populations throughout fine-grained ORS recovered from Rifle, Grand Junction, and Naturita, CO using functional gene markers for ammonia oxidation (*amoA*) and denitrification (*nirK*, *nirS*). Functional gene abundances are specifically targeted through qPCR, elucidating how relative numbers of nitrifiers and denitrifiers vary with depth and location and relate to uranium release in sediment cores. Sequence data obtained from Rifle indicate that subsurface archaeal *amoA* diversity spans the Group 1.1b *Thaumarchaeota*, and includes soil, freshwater, and estuarine relatives. Populations of *nirK*- and *nirS*-type denitrifiers have also been detected. These results indicate that robust communities of ammonia-oxidizing archaea (AOA) and denitrifiers coexist, both of which can produce nitrite.

We are using biogeochemical reactive transport modeling approaches to quantify the relationships among groundwater table variations and the production of nitrate, nitrite and U(VI) in diffusion-limited reduced zones, and the importance of the spatial distribution of these zones in determining aquifer-scale U(VI) concentrations. These results will integrate biogeochemical activity and uranium behavior observed in the field and laboratory, and provide critical guidance for future reactive transport experiments.

## SLAC SFA: Molecular pathways of U(VI) reduction in organic-rich sediments

**Program Affiliation:** Subsurface Biogeochemical Research

**Lead PI:** John Bargar<sup>1</sup> (bargar@slac.stanford.edu)

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The fate of redox-active radionuclides such as uranium, and biogeochemical critical elements (including C, N, S, and Fe), are profoundly affected by microbial processes in organic-rich sediments within floodplain aquifers. Accordingly, we are examining the processes that produce natural reduced zones (NRZs), which are usually manifested as thin, discontinuous tabular bodies. In particular, we are focusing on (i) syntrophic communities linking organic carbon degradation to metal reduction and (ii) the impacts of ligands that bind U(VI) and alter the reduction mechanism and U(IV) products within diffusive controls zones. This effort is also helping to elucidate the speciation of organic-associated U(IV) in uranium-contaminated floodplains.

The dominant source of reducing equivalents used in microbial respiration arises from particulate organic carbon (POC) inputs. Under the anaerobic conditions present in NRZs, a consortium of organisms is required to degrade POC, with hydrolytic enzymes providing soluble polymers that are decomposed by fermenters into products that fuel respiring organisms. We are examining the syntrophic relation in organic matter degradation linked to uranium (and iron) reduction using both natural consortia and isolates of the fermenter *Clostridium acidisoli* and the metal reducing bacterium *Geobacter metallireducens*. Utilizing advanced microspectroscopic methods coupled with microbial imaging (primarily fluorescence in situ hybridization), reaction products and the spatial organization of the consortia are being resolved within the complex subsurface matrices. For natural consortia, over a 9-week incubation, addition of POC as ground root tissue results in complete reduction of U(VI). Uranium(IV) resulting from microbially-mediated reduction are a combination of (primarily) complexed U(IV), with smaller amounts of uraninite (UO<sub>2</sub>). Uraninite formation is controlled by incubation time and initial U(VI) concentration, with longer incubation times and higher U(VI) concentrations favoring uraninite.

To establish the influence of U(VI) speciation, and U(IV) products, on the redox fate of uranium, we are using adsorptive stripping voltammetry (AdSV). By determining AdSV reduction potentials for compounds having known stability constants, values for unknown U(VI)-ligand complexes can be determined within simulated and natural subsurface systems. A range of U(VI) inorganic and organic ligands are being tested as well as natural organic matter plant extracts from the Upper Colorado River Basin. The combined assessment of U-ligand complexes and the syntrophic relation of microbial communities linking organic carbon degradation to metal reduction within complex physical environments of the subsurface will provide much needed information on the fundamental mechanisms controlling uranium, as well as carbon and nitrogen, fate in the subsurface.

## **SLAC SFA: Molecular mechanisms controlling oxidative release of uranium from organic-rich sediments: role of nitrification and denitrification**

**Program Affiliation:** Subsurface Biogeochemical Research

**Lead PI:** John R. Bargar<sup>1</sup> (bargar@slac.stanford.edu)

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**Affiliations:** <sup>1</sup>SLAC National Accelerator Laboratory, <sup>2</sup>Stanford University, <sup>3</sup>Lawrence Berkeley National Laboratory

Elevated U(IV) concentrations exist in fine-grained, organic-rich naturally reduced sediments in contaminated floodplains at ore processing sites across the upper Colorado River Basin. Recent evidence from Rifle, CO suggests that microbial nitrogen cycling is stimulated in organic-rich sediments by seasonal groundwater table fluctuations. Nitrate and nitrite produced by this activity are strong oxidants for U(IV). Consequently, there is concern that biogeochemical nitrogen cycling drives re-release of uranium from naturally reduced sediment zones (NRZs) to groundwater. The SLAC-SFA is investigating this subject using an integrated program of (i) laboratory incubation and column studies of Rifle sediments, (ii) studies of functional gene markers for nitrifying and denitrifying organisms, and (iii) biogeochemical reactive transport modeling.

Rifle NRZs were exposed to nitrate in diffusion-limited reactors. The greatest amount of aqueous U(VI) was released during the first two weeks of the experiment; however, solid-phase associated U(VI) continued to accumulate within 1 cm of the sediment-solution interface until the end of the experiment (70 days). Our work suggests that U(IV) oxidation by nitrate occurs on a time scale relevant to the field (ca. 2 – 3 months), but that release of aqueous U(VI) is diffusion-limited once the U(IV) at the sediment-solution interface is depleted. Experiments underway are investigating whether water-level fluctuations can promote nitrification of ammonium present in the sediments, causing seasonally elevated nitrate concentrations.

We are also investigating the diversity and abundances of nitrifying and denitrifying populations throughout NRZs recovered from Rifle, Grand Junction, and Naturita, CO using functional gene markers for ammonia oxidation (*amoA*) and denitrification (*nirK*, *nirS*). Functional gene abundances are specifically targeted through qPCR, elucidating how relative numbers of nitrifiers and denitrifiers vary with depth and location and relate to uranium release in sediment cores. Sequence data obtained from Rifle indicate that subsurface archaeal *amoA* diversity spans the Group 1.1b *Thaumarchaeota*, and includes soil, freshwater, and estuarine relatives. Populations of *nirK*- and *nirS*-type denitrifiers have also been detected. These results indicate that robust communities of ammonia-oxidizing archaea (AOA) and denitrifiers coexist, both of which can produce nitrite.

We are using biogeochemical reactive transport modeling approaches to quantify the relationships among groundwater table variations and the production of nitrate, nitrite and U(VI) in diffusion-limited reduced zones, and the importance of the spatial distribution of NRZs in determining aquifer-scale U(VI) concentrations. These results will integrate biogeochemical activity and uranium behavior observed in the field and laboratory, and provide critical guidance for future reactive transport experiments.

## **ANL Terrestrial Ecosystem Science SFA: Soil Organic Carbon Stocks and their Distributions across Ice-Wedge Polygons of Arctic Alaska**

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Gary Michaelson, University of Alaska Fairbanks

Estimates of the quantities of organic carbon stored in permafrost-region soils have improved immensely within the last few decades. However, uncertainties in these estimates remain high and affect our ability to reliably predict the vulnerability of the region's vast carbon stocks to remobilization caused by permafrost thaw and other perturbations related to climatic changes. Two major sources of uncertainty are (1) the uneven distributions and limited numbers of observational data, due to constraints on accessibility for much of this remote region; and (2) the high spatial heterogeneity of cryoturbated soils found in patterned ground — where freeze/thaw, frost heaving, and other cryogenic processes cause soil deformation, breaking/mixing of soil horizons, and deep burial of relatively labile organic matter. Ice-wedge polygons are ubiquitous throughout Arctic coastal plains and drainage basins. These patterned ground features are large enough (~5-30 m across) that a better three-dimensional understanding of their carbon stocks might improve geospatial upscaling of observational data. We investigated the horizontal and vertical (up to 3 m deep) distributions of soil organic matter across three polygon types on the North Slope of Alaska: low-centered (LCP), flat-centered (FCP), and high-centered (HCP) polygons, with each type replicated three times. We found variations in the thickness and quality of surface organic horizons for different polygon types. Below the active layer, organic-rich cryoturbated horizons were located in the transition zone and fingered down into the upper permafrost. The HCPs exhibited more prominent deformation than LCPs and FCPs. The cross-sectional distribution and heterogeneity of organic carbon density differed among polygon types, which led to type variations in overall polygon carbon stocks as well (HCP > LCP > FCP). Our findings suggest that an approach based on accounting for polygon-scale features (wedge to rim to center) and/or landscape-scale (polygon type) variations, in tandem with remote sensing and geospatial tools, could help constrain the uncertainties associated with upscaling of carbon stocks for areas of patterned ground dominated by ice-wedge polygons.

## **ANL Terrestrial Ecosystem Science SFA: Capturing the spatial heterogeneity of soil organic carbon stocks using soil-forming factors**

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Spatial heterogeneity of land surface affects energy, moisture, and greenhouse gas exchanges with the atmosphere. However, representing the spatial heterogeneity of terrestrial hydrological and biogeochemical processes in earth system models remains a critical scientific challenge. Here, we present a geospatial approach to capture the existing spatial heterogeneity of soil organic carbon (SOC) stocks across the State of Alaska. We used secondary information of soil-forming factors such as topography, climate, land cover types, and surficial geology to represent the spatial heterogeneity of SOC stocks. Using the standard deviation ( $38.2 \text{ kg C m}^{-2}$ ) of observed SOC stocks ( $n= 557$  existing pedons with sampled depths ranging from 0.3 to 4.5 m) and a margin of error 5% ( $\pm 2.5\%$ ), we calculated that 906 randomly distributed pedons would be needed to quantify the mean value of SOC stocks across Alaska. We used a conditioned Latin hypercube sampling approach to distribute the calculated number of pedons across Alaska in a manner that captured the spatial heterogeneity of soil forming factors. We then used the range of a variogram of observed SOC stocks to further refine the number of samples required to appropriately capture the spatial heterogeneity of SOC stocks across Alaska. Our results suggest 484 new observations would be needed to sufficiently quantify the spatial heterogeneity of Alaskan SOC stocks. Calculated variograms demonstrated that the spatial structures of soil-forming factors were appropriately captured by the identified sampling sites. However, given the difficulties and costs associated with accessing remote sites in Alaska, the total number of required observations could be reduced by accepting a greater margin of error (e.g., 227 pedons would be needed to capture the heterogeneity with a 10% margin of error). We also investigated whether stratifying our analyses by ecoregions within the State of Alaska would be a viable strategy for reducing both the margin of error and the required number of new observations. The results of this analysis will help to identify future sampling sites for research efforts that are intended to capture land surface heterogeneity and appropriately quantify Alaskan SOC stocks.

## **ANL Terrestrial Ecosystem Science SFA: Characterizing organic matter quality and lability of Alaskan soils using mid infrared spectroscopy**

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Chien-Lu Ping, University of Alaska Fairbanks

Soils in Arctic and sub-Arctic regions contain large amounts of organic matter that has been preserved in a relatively undecomposed state due to cold and often wet conditions, but the potential vulnerability of this organic matter to climate change is largely unknown. We are developing empirical tools for predicting the potential decomposability of organic C stored in these soils and for informing model development. In this study, we used diffuse-reflectance Fourier-transform mid-infrared spectroscopy (MidIR) to investigate soil organic matter (SOM) quality along a latitudinal gradient (78.79° N to 55.35° N) in Alaska and, in combination with soil incubations, to assess the lability of active-layer and upper permafrost SOM. The gradient encompassed 29 sites representing 10 vegetation types and 7 soil parent materials. Multiple soil horizons from each site were scanned to obtain MidIR spectra and were analyzed for organic and inorganic C, total N, particle size distribution, pH, cation exchange capacity, and exchangeable cations. Principal component analysis (PCA) of the MidIR spectra identified 20 bands that varied across vegetation type and parent material, with PCA axis one explaining 75.8% and 70.7% of the variation, respectively. Most of the identified bands were correlated with soil C concentrations. We found that single spectral bands could be relatively strong predictors of total organic C (2925), inorganic C (2512), Ca (1725), K (1226), and clay content (3675). Ratios of characteristic bands have been proposed in the literature as indicators of SOM quality or relative degradation state. We compared a suite of these band ratios and found that several were also indicative of SOM quality for the Alaskan soils. We also incubated active-layer organic and mineral soils and upper permafrost soils from selected tundra sites for 60 days at -1, 1, 4, 8 and 16 °C. Characteristic MidIR bands and band ratios identified via the latitudinal gradient were correlated with total CO<sub>2</sub> mineralized during the incubations. Several bands and band ratios (e.g., the ratio of lignin amides to lignin phenols) were significantly correlated with cumulative respired CO<sub>2</sub> as a function of incubation temperature, suggesting they might serve as useful lability indicators. Further investigation of these characteristic bands and band ratios for additional soils and for longer term incubations are needed to fully assess their utility as indicators of the relative degradation state and potential decomposability of permafrost-region soils.

## **LBNL Terrestrial Ecosystem Science SFA - Mysteries of the deep: Impact of warming on microbiology and carbon cycling in deep soils.**

Neslihan Tas, Eoin Brodie, Caitlin Pries, Cristina Castanha and Margaret Torn

In LBNL's Terrestrial Ecosystem Science SFA on soil carbon cycling, we conduct basic research on soil carbon turnover, storage, and loss. Our goal is to improve process-level understanding of biogeochemical dynamics and develop next-generation predictive capacity in global models of soils' role in ecosystem-climate interactions. Recent research demonstrates that environmental and biological controls are as important as soil organic matter (SOM) structure for SOM dynamics. To improve predictions of SOM response to climate change, this SFA aims to integrate this emerging understanding into soil carbon models by conducting strategically designed experiments and using observations to test and develop new model structures and parameters.

Soils store about 1,300–1,600 Pg organic carbon in the top meter. Despite their low carbon density, subsoil horizons contain more than half of global soil organic carbon, however while C turnover at depth is proposed to be slower than surface C, the vulnerability of deep soil carbon under future climate scenarios is yet to be understood. Microorganisms are responsible for both decomposition and formation of soil organic matter (SOM). The responses of microorganisms—changes in community composition, activity, gene expression, and physiology—determines how an environmental change will alter soil carbon and nutrient cycling. In this project, we aim to understand how long term warming impacts microbial community composition and decomposition of SOM in deep soils. To this end we established a soil warming experiment at the Blodgett Forest Research Station, located in the foothills of the Sierra Nevada, CA. The treatment warms the soil +4°C above ambient to >1 m depth while maintaining the natural temperature depth gradient. Samples across the soil profile were collected prior to the onset of warming and subsequently at six month intervals. Microbial community changes were analyzed via 16S rRNA gene sequencing and changes in microbial decomposition potential were assed via extracellular enzyme activity measurements for  $\beta$ -glucosidase (BG), cellobiohydrolase (CBH), N-acetyl- $\beta$ -D-glucosaminidase (NAG) and acid phosphatase (AP). Additionally lab incubations with  $^{13}\text{C}$  isotopologs of glucose and pyruvate were carried out to assess whether changes in microbial carbon use efficiency (CUE) occurred in response to warming. Although the activity of all enzymes declined with depth, when adjusted for mass of soil C total hydrolytic enzyme activity (CBH + BG + NAG) was similar across depths. NAG activity that also releases organic N, was higher than cellulose hydrolyzing enzymes (CBH, BG) in surface soils. While microbial composition and diversity varied significantly through the soil profile, with increases in bacteria with oligotrophic growth strategies with depth. Over the first six months soil warming did not significantly impact microbial composition and diversity; however incubations with  $^{13}\text{C}$ -labelled substrates demonstrated a 2-3 fold increase in respiration due to warming. Metabolic modeling is being carried out to determine whether microbial CUE profiles correspond to microbial composition across the soil profile if CUE varies in response to warming.

## Abstract

MS Torn, Caitlin Hicks Pries, Rose Abramoff, Katerina Georgiou, Rachel C. Porras, Cristina Castanha, Eoin Brodie, Neslihan Tas, Peter Nico, Bill J. Riley.

**Title:** LBNL Terrestrial Ecosystem Science SFA: Belowground carbon cycling

TEXT: In LBNL's Terrestrial Ecosystem Science SFA on soil carbon cycling, we conduct basic research on soil carbon turnover, storage, and loss. Our goal is to improve process-level understanding of biogeochemical dynamics and develop next-generation predictive capacity in global models of soils' role in ecosystem-climate interactions. Recent research demonstrates that environmental and biological controls are as important as soil organic matter (SOM) structure for SOM dynamics. To improve predictions of SOM response to climate change, this SFA aims to integrate this emerging understanding into soil carbon models by conducting strategically designed experiments and using observations to test and develop new model structures and parameters.

This poster will feature results from the whole-profile soil warming experiment. Over half of global soil organic carbon (SOC) is stored in subsurface soils >30 cm deep. While most climate experiments have only warmed surface soils, we are warming (+4°C) a coniferous forest soil *in situ* to 1 m. Warming began in October 2013. It has increased surface soil respiration by 40% relative to the control and increased concentrations of dissolved organic carbon as well. In addition to these biogeochemistry results, we are also applying a combination of field and laboratory experiments, microbial ecology, advanced imaging, and numerical simulation modeling in tasks on, for example, microbial carbon use efficiency, SOM stabilization via organo-mineral interactions; and soil biogeochemical modeling.

## **LBLN TES SFA: Emergent responses of soil C dynamics to seasonal variability in nonlinear SOM-microbial models**

Katerina Georgiou (kgeorgiou@berkeley.edu), UC Berkeley; William J. Riley (Co-PI), LBNL; Jinyun Tang, LBNL; Margaret S. Torn (PI), LBNL.

Soil organic matter (SOM) decomposition is regulated by biotic and abiotic processes. Interactions between these processes may dampen oscillatory responses to perturbations. Indeed, although biological oscillations have been observed in small-scale laboratory incubations, plot-scale behavior often exhibits a relatively stable response to disturbances in input rates and temperature. Recent studies have demonstrated the ability of microbial models to capture nonlinear feedbacks in SOM decomposition that linear Century-type models are unable to reproduce, such as soil priming in response to increased carbon input. However, these microbial models often exhibit strong oscillatory behavior that is deemed unrealistic. The inherently nonlinear dynamics of SOM decomposition have important implications for global climate-carbon and carbon-concentration feedbacks. It is therefore imperative to represent these dynamics in Earth System Models (ESMs) by introducing sub-models that accurately represent microbial and abiotic processes.

In this LBNL TES SFA modeling study we explore, both analytically and numerically, microbe-enabled model structures of varying levels of complexity. The most complex model combines microbial physiology, a non-linear mineral sorption isotherm, and enzyme dynamics. Based on detailed stability analysis of the nonlinear dynamics, we calculate the system modes as functions of model parameters. This dependence provides insight into the source of state oscillations. We find that feedback mechanisms that emerge from explicit representation of enzyme and mineral interactions, with parameter values in a prescribed range, are critical for both maintaining system stability and capturing realistic responses to disturbances. Furthermore, we explore the effect of forcing microbial models with periodic temperature and carbon inputs, and conclude that the frequency at which the system is resolved can greatly influence the dynamics. This observation has important implications for comparing model predictions to field studies and laboratory incubations. Corroborating and expanding upon the results of recent studies, we discuss the appropriate microbe-enabled model structure for inclusion in ESMs.

**Explicitly representing microbes, enzymes, mineral interactions, and tracer transport to predict depth-resolved SOM stocks and turnover under warming: A component of the LBNL TES SFA**

W.J. Riley, D. Dwivedi, K. Georgiou, J. Tang, M.S. Torn

Recent work by our and other groups indicates that emergent soil organic matter dynamics depends on microbes, enzymes, and mineral surface interactions. As part of the LBNL TES SFA in Belowground Carbon Cycling, we are developing and applying models that explicitly represent microbial physiology, thermodynamic constraints on uptake, internal physiology, and surface complexation with mineral surfaces. Our enzyme submodel accounts for production, interactions with dissolved organic substrates, and surface complexation. Temperature sensitivities of the various processes are separately represented and are being integrated into the existing reactive transport solver in CLM4.5. We have also integrated these results into the reactive transport solver TOUGHREACT, and will present results demonstrating that this model structure can accurately predict vertically resolved SOM stocks and  $\Delta^{14}\text{C}$  values across a mineralogical gradient. We also show that these complex interactions result in non-intuitive functional dependencies that cannot be calibrated, implying that directly simulating SOM dynamics requires explicit representation of these processes.

**ORNL's Terrestrial Ecosystem Science – Scientific Focus Area (TES SFA)  
A 2015 Overview**

Paul J. Hanson, Daniel M. Ricciuto and Project Participants  
Climate Change Science Institute, Oak Ridge National Laboratory  
Oak Ridge, Tennessee

Understanding responses of ecosystem carbon (C) cycles to climatic and atmospheric change is the aim of the Terrestrial Ecosystem Science Scientific Focus Area (TES SFA). Our vision is to:

**Improved integrative understanding of terrestrial ecosystem processes to advance  
Earth System predictions through experiment-model-observation synergy**

The TES SFA is guided by the vision that sensitivities, uncertainties and recognized weaknesses of Earth System Model (ESM) predictions inform observations, laboratory and field experiments and the development of ecosystem process modeling. In turn, predictive understanding and findings from the field and laboratory and improved process modeling are incorporated (with the associated uncertainties) into ESMs as explicitly and expeditiously as possible. Overarching science questions are:

- (1) How will atmospheric and climate change affect the structure and functioning of terrestrial ecosystems at scales from local to global and from decadal to centuries?
- (2) How will fossil fuel emissions and terrestrial ecosystem processes, mechanisms, interactions and feedbacks control the magnitude and rate of change of atmospheric CO<sub>2</sub> and other greenhouse gases?
- (3) What are the climate change-induced shifts in terrestrial hydrologic and ecosystem processes that inform assessment of climate change impacts on ecosystem services and society?

The proposed science includes large manipulations, C-Cycle observations, database compilation, and process studies integrated and iterated with modeling activities. The centerpiece of our climate change manipulations is the SPRUCE experiment testing multiple levels of warming at ambient and elevated CO<sub>2</sub> on the C feedbacks from a black spruce–*Sphagnum* ecosystem. Other TES SFA efforts aim to improve mechanistic representation of processes within terrestrial biosphere models by furthering our understanding of fundamental ecosystem functions, and their response to environmental change. The TES SFA aims to integrate experimental and observational studies with model building, parameter estimation, and evaluation to yield reliable model projections. This integrated model-experiment approach fosters an enhanced, interactive, and mutually beneficial engagement between models and experiments to further our predictive understanding of the terrestrial biosphere.

## **SPRUCE Deep Peatland Heating: System Performance and Measured “Ecosystem” Net Surface CO<sub>2</sub> and CH<sub>4</sub> Responses**

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Deep soil heating infrastructure was completed in 2014 for a peatland whole-ecosystem warming study that will include air warming starting in 2015 (SPRUCE; <http://mnspruce.ornl.gov>). In June 2014, deep soil heating was initiated to test the responsiveness of deep peat carbon stocks, microbial communities and biogeochemical cycling processes to heating at 4 warming levels (+2.25, +4.5, +6.75 and +9 °C; 2 replicate plots) compared to fully-constructed control plots (+0 °C; 2 replicate plots). The warming treatments were deployed over eight 113 m<sup>2</sup> areas using circular arrays of low-wattage (W) electrical resistance heaters. With an average peat depth of 2.5 meters this system was able to warm approximately 113 of the 282 m<sup>3</sup> of peat within each target plot. In the absence of the air warming cap, *in situ* deep peat heating is only effective at sustaining warming in the deep peat layers. Warming levels at depth were achieved over a 25-day (+ 2.25 °C) to a 60-day (+9 °C) period depending on the target treatment temperatures in agreement with a priori energy balance model simulations. Initial biological and biogeochemical responses to these manipulations are being actively assessed. The mild and gradual warming treatments took several months to produce enhanced levels of net CH<sub>4</sub> flux for the treatment plots proportionate to measured levels of deep peat warming. The enhanced levels were only maintained during the warm growing season, and dropped to near zero when surface conditions were frozen. Other data suggest that CH<sub>4</sub> generation within the peat column may be limited to current photosynthate supplies that become limited in the cold portion of the year. Limited surface aerobic zones did not produced enhanced net dark CO<sub>2</sub> fluxes from the plots, but this pattern is expected to change with whole-ecosystem warming in 2015. Late winter and pre-thaw assessments of belowground CO<sub>2</sub> and CH<sub>4</sub> production are scheduled for April 2015. They are expected to provide insights into deep peat responses to sustained and historically unprecedented warming.

## **Title: Responses of peat porewater chemistry to deep peat warming in a northern peatland**

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### **Abstract**

Northern peatlands store over 30% of the world's terrestrial carbon, and evaluating the responses of these peatland ecosystems to warming is critical for understanding carbon cycle feedbacks and effects on associated biogeochemical cycles. The Spruce and Peatland Responses Under Climatic and Environmental change (SPRUCE) experiment is assessing the response of a black spruce-*Sphagnum* bog ecosystem (S1 bog at the Marcell Experimental Forest in northern Minnesota) to warming (+0, +2.25, +4.5, +6.75, and +9°C) and elevated CO<sub>2</sub> concentrations (800-900 ppm). The treatments will be imposed within ten 12-m diameter, open-topped chambers for 10 years, using infrastructure that warms both above and belowground to achieve whole-ecosystem warming. Within the SPRUCE experiment, we are characterizing the depth profiles of porewater chemistry (0 to 3 m into the peat) with the goal of understanding how solute concentrations and yields, particularly total organic carbon (TOC), respond to warming and elevated CO<sub>2</sub>. This information will aid in assessing nutrient cycling, decomposition, and organismal responses and will be critical to interpreting the sources, cycling, and transport of organic matter from the peatland.

In June 2014, belowground warming ('deep peat heating') was initiated to evaluate the responses of deep peat soils (warming targeted at 2 m depth; 4000-7000 year old peat). We measured the chemistry of porewater every 2 weeks both before and during warming in all 10 plots. We predicted that TOC concentrations would increase with warming due to mineralization of deep peat at 2 m, with potential cascading effects to coupled biogeochemical cycles (i.e., increased ammonium concentrations due to mineralization). Plots reached their target heating levels between July and mid-September 2014. Total organic carbon concentrations increased by approximately 15% in the +6.75°C and +9°C treatments by the end of the sampling period (October/November 2014). In comparison, TOC concentrations in the lower temperature treatments (+0°C, +2.25°C, +4.5°C) only increased by 2%. Similar responses of porewater TOC were not observed at 1 m suggesting that elevated TOC may be a response to deep peat heating rather than a natural temporal pattern that occurred in the warmer temperature treatment plots. There were no changes in porewater pH and specific conductivity (at 2 m) with deep peat heating. Analysis of porewater samples for nutrients (ammonium, nitrate, phosphate), cations, and anions is ongoing, and responses of these solutes to deep peat heating will also be presented.

## **Just beneath the surface: The distribution and dynamics of fine roots in a forested peat bog**

*Terrestrial Ecosystem Sciences Program*

*Oak Ridge National Laboratory TES Science Focus Area (PIs Hanson and Ricciuto)*

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Fine plant roots, which are narrow-diameter, ephemeral roots responsible for plant water and nutrient acquisition, contribute to wetland carbon dioxide and methane fluxes through respiration, exudates of labile carbon compounds, input of root detritus, and the presence of aerenchyma. However, the distribution and dynamics of fine roots have rarely been examined in wetlands, in part because of methodological difficulties associated with cold, saturated soils. Our objective was to determine the production of ephemeral roots throughout the soil profile in an ombrotrophic bog that is the location of the Spruce and Peatland Responses Under Climatic and Environmental change (SPRUCE) experiment (<http://mnspruce.ornl.gov/>). We used several methods to characterize ephemeral roots, including species-specific sampling to investigate the relationships among root order, root morphology, and root chemistry; minirhizotrons installed across gradients of tree density and microtopography to quantify root production and mortality throughout the peat profile; in-growth cores to quantify the chemistry and morphology of newly-produced roots; peat cores to determine rooting depth distribution; and novel, automated minirhizotron technology to track the dynamics of ephemeral roots and mycorrhizal hyphae at high spatial and temporal resolution. The common vascular plant species in the bog encompassed a range of root morphology, diameter distributions, and mycorrhizal colonization. Across a range of root orders, root diameter was strongly related with root mass per length and root nitrogen concentration. Root phenology was bimodal for both trees and shrubs; the first peak in production occurred early in the growing season before peak leaf and woody growth, and the second peak occurred late in the growing season after needle expansion was complete and peak woody growth was past. Root standing crop and production were greater in raised hummocks than in saturated hollow depressions, and living roots were generally confined to the aerobic zone above the average summer water table level. Well-preserved dead shrub roots were found in peat samples as deep as 2 m, with a calibrated <sup>14</sup>C age of ~5000 years. Similarly, fungal hyphae occurred only in shallow peat. These measurements are being used to parameterize ecosystem and land surface models to refine hypotheses regarding the expected effects of warming and elevated CO<sub>2</sub> on root distribution, dynamics, and carbon and nitrogen cycling in globally important peatland ecosystems.

Beginning in 2015, the Spruce and Peatland Responses under Climatic and Environmental Change (SPRUCE) climate change experiment (<http://mnspruce.ornl.gov/>) in Northern Minnesota, USA, will expose 13 m diameter plots of an ombrotrophic *Picea mariana* – *Ericaceous* shrub – *Sphagnum* bog ecosystem to long-term temperature × CO<sub>2</sub> treatments. Treatments are expected to change soil water availability, vapor pressure deficit, photosynthesis, respiration, evapotranspiration and relative species composition. We examined pre-treatment ecophysiology of *Picea mariana* (black spruce) including seasonal assessment of cohort specific light-saturated assimilation rate ( $A_{max}$ ), maximum electron transport rate ( $J_{max}$ ), maximum carboxylation capacity ( $V_{cmax}$ ), respiration and their temperature response functions. In addition, we assessed diurnal and seasonal patterns of sap flow and species-specific patterns of water potential. Granier-style thermal dissipation probes (TDP) were calibrated *in situ* by cutting instrumented trees and measuring their actual water uptake. We also assessed spruce hydraulic conductivity under drying conditions in excised roots, branches and foliage using vulnerability curves and pressure-volume curves.

Photosynthetic capacity increased as the season progressed, and peaked by late summer, with the 1-2 year old cohorts contributing more than new needles to modeled total C uptake.  $V_{cmax}$  and  $J_{max}$  were not responsive to T in the spring, however, by August they were highly sensitive to T, with optimal T peaking between 35-38°C, slightly higher than current maximum summer air T. The SPRUCE experimental treatments will push air T up towards 45°C in some plots, which will allow us to test foliar capacity for biochemical T acclimation. Sap flow began by late May and was fairly constant over the season until declining in mid-September and ceasing as temperatures dropped below zero. The *in situ* calibrations improved sap flow estimates, and illustrated substantial hysteresis in sap flow due to release of stored water in larger trees. Midday mean summer  $\psi$  was -1.5 MPa for spruce foliage, higher than the co-occurring *Larix laricina* (larch), which was -2.0 MPa. Laboratory measurements indicated specific leaf conductivity of spruce declined as drought stress increased beyond -1.2 MPa, with the average turgor loss point (TLP) reached by -2.5 MPa, lower than the TLP of larch (-1.95 MPa). While summer spruce  $\psi$  remained higher than the TLP, larch often reached the TLP indicating substantial loss of hydraulic conductivity on a daily basis, indicating potential for shifts in community composition due to treatment effects on net carbon uptake and differential water stress among the species.

# Representing northern peatland microtopography and hydrology within the Community Land Model

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## **Abstract**

Predictive understanding of northern peatland hydrology is a necessary precursor to understanding the fate of massive carbon stores in these systems under the influence of present and future climate change. Current models have begun to address microtopographic controls on peatland hydrology, but none have included a prognostic calculation of peatland water table depth for a vegetated wetland, independent of prescribed regional water tables. We introduce here a new configuration of the Community Land Model (CLM) which includes a fully prognostic water table calculation for a vegetated peatland. Our structural and process changes to CLM focus on modifications needed to represent the hydrologic cycle of bogs environment with perched water tables, as well as distinct hydrologic dynamics and vegetation communities of the raised hummock and sunken hollow microtopography characteristic of peatland bogs. The modified model was parameterized and independently evaluated against observations from an ombrotrophic raised-dome bog in northern Minnesota (S1-Bog), the site for the Spruce and Peatland Responses Under Climatic and Environmental Change experiment (SPRUCE). Simulated water table levels compared well with site-level observations. The new model predicts significant hydrologic changes in response to planned warming at the SPRUCE site. At present, standing water is commonly observed in bog hollows after large rainfall events during the growing season, but simulations suggest a sharp decrease in water table levels due to increased evapotranspiration under the most extreme warming level, nearly eliminating the occurrence of standing water in the growing season. Simulated soil energy balance

was strongly influenced by reduced winter snowpack under warming simulations, with the warming influence on soil temperature partly offset by the loss of insulating snowpack in early and late winter. The new model provides improved predictive capacity for seasonal hydrological dynamics in northern peatlands, and provides a useful foundation for investigation of northern peatland carbon exchange.

## **Sensitivity of Community Land Model land-surface fluxes and biomass to carbon-cycle parameters**

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Incomplete knowledge about ecological processes contributes to substantial uncertainties in climate change projections. Global land surface models and Earth system models used to make climate projections are computationally expensive and contain large numbers of parameters representing ecological processes, limiting the feasibility of uncertainty quantification (UQ) studies that require large model ensembles. Fortunately, even relatively small model ensembles can yield useful information about key model parameter sensitivities. Model parameters are often linked to key ecosystem traits. Knowledge about how these traits are distributed and how they drive carbon and water cycles is of key importance to not only the modeling community, but also the measurement community as this knowledge can inform observation strategies targeted at reducing prediction uncertainties. In this study, we determine the ranking of parameter importance by applying the Morris method on Community Land Model (CLM) model parameters at AmeriFlux sites. We then perform a variance-based analysis to provide a way of analyzing the contributions (linear and non-linear) by each parameter and its interactions with other parameters to the variance of the model output. Particular model outputs of interest are biomass, net carbon fluxes and energy fluxes.

We find that the ranking of parameter importance strongly depends on the plant functional type and environmental drivers. The parameterization of mortality, rooting depth, photosynthesis and stomatal conductance is particularly important and regulates total biomass and seasonal patterns of carbon exchange in these ecosystems. We also evaluate the performance of the model against measured eddy covariance data and determine which combinations of parameters are most likely given the observations.

## Improving Soil C Dynamic Models Through the Incorporation of Microbial Processes

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The focus of our research is to develop robust parameters and an improved conceptual understanding of microbial-facilitated decomposition of organic matter, and apply these to improve model representation of microbial decomposition using the Microbial ENzyme Decomposition (MEND) Model. We used incubation-derived experimental data to calibrate MEND, where calibration targets were CO<sub>2</sub> fluxes from native soil C, <sup>14</sup>CO<sub>2</sub> fluxes from substrate additions, microbial biomass carbon (MBC), and dissolved organic carbon (DOC). We found that predicted MBC values were substantially less than measured at 150 days and longer, which we attributed to unaccounted dormancy in the microbial community. We developed a microbial physiological model to account for both dormant and active fractions, and refined the MEND decomposition model. The new model improved the simulation of MBC values, but further testing of simulated microbial growth and maintenance rates required greater temporal resolution of MBC and CO<sub>2</sub> fluxes. Therefore, we are performing a new set of incubations with a detailed series of short-term measurements (0, 2, 4, 8, 24, 48, 72, 96, 120, 144 h) using <sup>13</sup>C glucose addition, and long-term measurements (0, 1, 2, 4, 6, 10, 20, 38, 60, 90...730 d) using <sup>13</sup>C cellulose addition. Specifically, the maximum specific growth and maintenance rates, the Michaelis-Menten half-saturation constant, the initial active fraction in microbes, and the growth yield efficiency can be calibrated from short-term data and applied to long-term data. Furthermore, because MEND currently uses only one C pool for microbes (MBC) and does not have the capability to capture microbial community dynamics, we tested alternate measures of MBC, including quantitative PCR (QPCR), phospholipid fatty acid analysis (PLFA), and direct counts, which would facilitate modeling simple forms of community dynamics. We have identified good correlations between MBC, QPCR, and PLFA that are substantially stronger than relationships between MBC and soil physical parameters such as moisture, temperature, or texture. This suggests that QPCR or other data may be substituted for MBC in future model calibration targets, with the added advantage of providing better information on microbial community composition and greater scalability for data generators. Paired forest and grassland soils were collected from four sites including Alfisols in Missouri near MOFLUX and Athens OH, Ultisols from the Freel's Bend site in TN, and Mollisols from the Chichaqua Bottoms Greenbelt site in IA. These incubation experiments will allow us to test and calibrate the MEND model, but also explore how microbial community dynamics can be incorporated into future versions of the MEND model.

## **Influence of phosphorus cycle coupling on land model response to CO<sub>2</sub> fertilization and climate variability**

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It is being increasingly recognized that carbon-nutrient interactions play important roles in regulating terrestrial carbon cycle responses to increasing CO<sub>2</sub> in the atmosphere and climate change. Nitrogen-enabled models in CMIP5 indicated that the inclusion of nitrogen cycle reduces CO<sub>2</sub> fertilization effect and warming-induced carbon loss from land ecosystems. None of the CMIP5 models has considered phosphorus (P) as a limiting nutrient. Phosphorus has been commonly considered to be the most limiting nutrient in lowland tropical forests. Only recently a few land models have considered P dynamics and C-N-P interactions (CASA-CNP, JSBACH-CNP and CLM-CNP) and these models show strong P limitation in tropical forest responses to increasing atmospheric CO<sub>2</sub>. In this study, we have performed a set of offline global-scale simulations using CLM-CNP constrained by realistic maps of phosphorus distribution. We examine the influence of including phosphorus cycle dynamics and C-N-P interactions on C-climate feedbacks. We illustrate the spatial patterns of dominant nutrient limitation (N-limited vs. P-limited) on the global scale. We show that P-limitation dominates over most of the tropics and sub-tropics, while N limitation dominates over most of the temperate and high-latitude regions. We also show that phosphorus cycle coupling reduces the sensitivity of net carbon exchange to variations in both temperature and precipitation.

**Climate variability as a key factor for model improvement: insights from observed and modeled ecosystem functional responses to precipitation regimes and associated stresses in a central US forest**

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## **Abstract**

Terrestrial carbon and water cycles exhibit large interannual variabilities at scales from local and global. The causes of such variabilities have not been well understood and our current capacity to model them is limited. In this study, we related the observed and modeled interannual variabilities of carbon uptake and evapotranspiration at the Missouri Ozark AmeriFlux site in the central USA to corresponding climate variability. We showed that precipitation regimes and associated water and heat stresses determined seasonal and interannual variations of carbon uptake and water use in this deciduous forest ecosystem and these effects were captured with a few simply constructed climate variability indices. While the interannual fluctuation in carbon uptake was large, a net carbon sink was maintained even during an extreme drought year, suggesting a high degree of resilience of this forest ecosystem to atmospheric stresses. The Community Land Model (CLM) predicted seasonal and interannual variations in evapotranspiration reasonably well. However, its predicted carbon uptake was too small across the observed range of climate variability. Also, the model systematically underestimated the sensitivities of carbon uptake and evapotranspiration to climate variability and overestimated the coupling between carbon and water fluxes. We suggest that future model improvements should focus on better representation and parameterization of process responses to atmospheric stresses and more complete representations of carbon-specific processes such as mesophyll diffusion.

**Key words:** Carbon and Water Fluxes, Climate Variability Indices, Land Surface Modeling, Eddy Covariance, Climate Change

1 **Predictors and mechanisms of the drought-influenced mortality of tree species along**  
2 **the isohydric to anisohydric continuum in a decade-long study of a central US**  
3 **temperate forest**

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32 **Abstract**

33 Using decade-long continuous observations of tree mortality and predawn leaf water  
34 potential ( $\psi_{pd}$ ) at the Missouri Ozark AmeriFlux (MOFLUX) site, we studied how the  
35 mortality of important tree species varied along the isohydric to anisohydric continuum  
36 and how such variations may be predicted. Water stress determined inter-annual  
37 variations in tree mortality with a time delay of one year or more, which was predicted by  
38 predawn leaf water potential integral (PLWPI), mean effective precipitation interval (a  
39 time period with no daily precipitation rates exceeding a threshold) with a daily threshold  
40 precipitation at 5 mm day<sup>-1</sup> (MEPI5), and precipitation variability index (PVI). Positive  
41 temperature anomaly integral (PTAI) and vapor pressure deficit integral (VPDI) also  
42 worked reasonably well, particularly for moderate droughts. The extreme drought of the  
43 year 2012 drastically increased the mortality of all species in the subsequent year.  
44 Regardless of the degree of isohydry and drought intensity, the  $\psi_{pd}$  of all species  
45 recovered rapidly after sufficiently intense rain events. This, together with a lack of  
46 immediate leaf and branch desiccation, suggests that hydraulic disconnection in the  
47 xylem was absent even during extreme drought and tree death was caused by significant  
48 but indirect effects of drought. We also found that species occupying middle positions  
49 along the isohydric to anisohydric continuum suffered less mortality than those at either  
50 extremes (i.e., extremely isohydric or extremely anisohydric). Finally, our study  
51 suggested that species differences in mortality mechanisms can be overwhelmed and  
52 masked in extreme droughts and should be examined in a broad range of drought  
53 intensity.

54 **Key words:** Drought, isohydric, anisohydric, predawn leaf water potential, tree mortality  
55 predictors

A Scientific Function Test Framework for Modular Environmental Model Development:  
Application to the Community Land Model

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Environmental system modeling presents a variety of challenges. Through the past several decades, along with strong interests of understanding the large-scale environmental phenomena and the rapid development of computing technologies, many computer models have been developed to capture our knowledge on numerous facts of environmental systems, and to explore better options for system-wide management. Therefore, environmental models generally embrace multiscale and multidisciplinary integration. Recently, many high performance, integrated environmental modeling systems have been developed to address new challenging problems. It is challenging to redesign environmental models and to validate model results under new configurations, because the software system of these environmental models quickly becomes complicated. Therefore, we need new tools to analyze and verify model projections, to expedite integrated model developments, and to facilitate the collaborations among broad scientific communities including field scientists, environmental system modelers and computer scientists

From a software engineering perspective, a lot of effort has been placed on software structure analysis to improve software quality and computing performance. We think it is the time to develop new computational frameworks to analyze complicated environmental modeling system with emphasis on hypotheses, scientific workflow, and numerical methods inherited from existing model development. Herein, we present our new effort on scientific function test framework for modular environmental model development. Evolved from the traditional concepts on software unit testing, our framework is designed to provide innovative and convenient (piece-by-piece) ways for process-based multiscale model verification and validation, covering both model structure and scientific workflow. It expedites model modification and enhancement; it also enables environmental model reconfiguration, reuse and reassembly. We have applied these methods to the Community Land Model with three typical scenarios: 1) benchmark case function validation, 2) observation-constraint function validation, and 3) a virtual root module generation for root function investigation and evaluation. We believe that our strategies and experience in scientific function test framework can be beneficial to many other research programs that adapt integrated environmental modeling methodology.

## The Impact of Elevated CO<sub>2</sub> on Plant Production Responses to Drought: A Model–Data Comparison at Four US FACE Sites.

Anthony Walker, Lynn Fenstermaker, Martin De Kauwe, Belinda Medlyn, Elise Pendall, Sönke Zaehle, Rich Norby, and the FACE–MDS team.

Plants respond to increasing atmospheric CO<sub>2</sub> (eCO<sub>2</sub>) by reducing stomatal apertures which, coupled with increased assimilation rates, increases plant water use efficiency (WUE). In some environments, increased WUE allows for water savings that can prolong the onset of detrimental drought effects on plants.

Ecosystem observations from four long-term Free-Air CO<sub>2</sub> Enrichment (FACE) experiments—the evergreen needleleaf Duke Forest FACE experiment (NC), the deciduous broadleaf Oak Ridge FACE experiment (TN), the prairie heating and FACE experiment (WY), and the Nevada desert FACE experiment—were used to evaluate the assumptions of a suite of terrestrial ecosystem models.

All sites experienced at least one dry year which coincided with below average annual net primary production (NPP). At all but the driest site (NV), eCO<sub>2</sub> alleviated the effect of the dry year on NPP, the extent of which increased with how mesic the site was in general. Many models were able to capture this response across sites though there substantial differences in model behaviour. Model assumptions that were important in determining the under eCO<sub>2</sub> mediated recovery of NPP during the dry year were: The soil water content at which soil water becomes limiting to plants; whether soil water limitation affects stomatal conductance, photosynthetic parameters, or both; and the shape of the soil water limitation curve.

## **Temporal, Spatial, and Uncertainty Aspects of Carbon Dioxide Emissions from Fossil Fuel Combustion: Highlights of the Last Year of TES Funding**

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Continued TES funding has led to improvements in understanding fossil fuel carbon dioxide (FFCO<sub>2</sub>) emissions, especially in terms of their temporal distribution, spatial distribution, and uncertainties associated with those emissions. Research continues in all three of these areas with TES support.

Temporally, monthly inventories of FFCO<sub>2</sub> emissions have been completed from January 1950 to December 2010. Emission year 2011 data are being calculated at the time of this writing. Nations are the basic spatial unit of data (which can be summed to global totals). One of the primary results of this research is the global monthly time series is statistically different from a uniform annual distribution.

Spatially, the annual and monthly data are gridded at one degree latitude by one degree longitude. This data format has proven so useful to the broader community that others have made attempts to improve upon the gridding methodology originally published in 1996 (Andres et al., *Global Biogeochem. Cycles* 10:419-429). Each of these gridding attempts suffer from spatial, temporal and/or coverage uncertainties.

Research on uncertainties associated with FFCO<sub>2</sub> emissions has been concentrated in global totals and gridded distributions. A new global uncertainty analysis has been published (Andres et al., 2014, *Tellus B*, 66, 23616. doi:10.3402/tellusb.v66.23616). The analysis includes three separate uncertainty assessments, resulting in a multifaceted examination of the uncertainty associated with FFCO<sub>2</sub> emission estimates. The three assessments collectively give a range that spans 1.0 to 13% (2 sigma). Greatly simplifying the assessments to obtain one value gives a global FFCO<sub>2</sub> uncertainty value of 8.4% (2 sigma).

Uncertainty assessments on gridded distributions are nearing publication. Individual component uncertainties from geography, national emission estimates, and distribution proxies have been considered.

Future work will continue efforts already begun as well as make a renewed push to better integrate FFCO<sub>2</sub> emissions into our understanding of the terrestrial biosphere. A. W. King will lead these efforts. Currently under consideration is how variations in atmospheric <sup>13</sup>C might introduce uncertainty in <sup>13</sup>C as a tracer of carbon transfers in the biosphere.

Peer-reviewed publication of this work continues. Since the last TES presentation one year ago, TES funding has contributed to five major publications as well as meeting abstracts, presentations, and interactions. Also of note are a contributing authorship to IPCC AR5 Working Group III chapter 5, preliminary efforts toward the Coupled Model Intercomparison Project Phase 6 (CMIP6) activities, the Global Carbon Project Global Carbon Atlas (<http://www.globalcarbonatlas.org>), and press interactions.

## ORNL's TES SFA Data Management in Support of MODEX to Facilitate Data Sharing and Analyses

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Data management, sharing, and archiving are an integral part of the ORNL TES SFA. The open sharing of all data and results from SFA research and modeling tasks among investigators, the broader scientific community, and the public is critical to advancing the mission of DOE's Program of Terrestrial Ecosystem Science. TES SFA researchers are developing and deploying the data systems, repositories, tools, and integration capabilities needed for the collection, storage, processing, sharing, analysis, and archiving of data and model products.

These capabilities facilitate model-data integration and provide accessibility to model output and benchmark data for analysis, visualization, and synthesis activities in support of the TES SFA Vision. Active data sharing facilitates delivery of SFA products to sponsors, the scientific community, and the public. Task specific web sites, access to web-based tools, links to external products (e.g., microbial metagenomes), and data center value-added products (<http://tes-sfa.ornl.gov/>) enable these interactions.

The SPRUCE experiment (Spruce and Peatland Responses under Climatic and Environmental Change) is a key component of the SFA. SPRUCE is implementing an experimental platform for the long-term testing of the mechanisms controlling the vulnerability of organisms, ecosystems, and ecosystem functions to increases in temperature and exposure to elevated CO<sub>2</sub> treatments within the northern peatland high-carbon ecosystem. All data collected at the SPRUCE facility, all results of analyses or synthesis of information, and all model algorithms and codes developed in support of SPRUCE will be submitted to the SPRUCE Data Archive in a timely manner such that data will be available for use by SPRUCE researchers and, following publication, the public (<http://mnspruce.ornl.gov>).

This poster highlights ORNL TES SFA tasks including data acquisition system development, data products, web-based tools, and their availability to project staff and the public.

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