

Program and Abstracts

for the

2014 Joint Terrestrial Ecosystem Sciences and Subsurface Biogeochemical Research Principal Investigators (PI) Meeting

Bolger Center
Potomac, MD
May 6-7, 2014

Climate and Environmental Sciences Division (CESD)
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Welcome

Welcome to the 2014 Joint Terrestrial Ecosystem Science (TES) and Subsurface Biogeochemical Research (SBR) Principal Investigators (PI) meeting! This program and abstract document provides a record of the research sponsored by the TES and SBR activities within the Climate and Environmental Sciences Division (CESD) of the Department of Energy's Office of Biological and Environmental Research.

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 May 6-7, 2014 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. Challenges and needs associated with scaling are common themes of both programs and are reflected in the meeting agenda. The poster session includes 10 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.

The AmeriFlux annual PI meeting took place immediately prior to this Joint Investigators meeting and many of the AmeriFlux PIs will also be present at this meeting in their role as scientists funded by our programs. This is the first time we have connected the AmeriFlux meeting with the Joint Investigators meeting and we encourage the communities to interact to explore new opportunities for collaboration.

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 CESD and Jody Crisp and Tracey Vieser of ORISE for coordinating the logistical aspects and arrangements for the meeting.

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

May 6, 2014

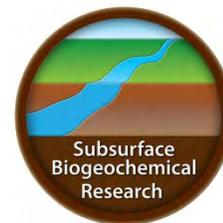
Table of Contents

<i>Welcome</i>	<i>iii</i>
<i>Table of Contents</i>	<i>iv</i>
<i>Agenda</i>	<i>v</i>
<i>Venue Map</i>	<i>xi</i>
<i>Presentation Abstracts</i>	<i>xii</i>
<i>Poster Abstract List</i>	<i>lv</i>
<i>SBR Poster Abstracts</i>	<i>19</i>
<i>Early Career Awards</i>	<i>19</i>
<i>Institute</i>	<i>21</i>
<i>Scientific Focus Areas (SFA)</i>	<i>22</i>
<i>Student Abstracts</i>	<i>60</i>
<i>University-Led Research</i>	<i>65</i>
<i>TES Poster Abstracts</i>	<i>95</i>
<i>Ameriflux</i>	<i>95</i>
<i>Early Career Awards</i>	<i>100</i>
<i>Federal Agency-Led Research</i>	<i>102</i>
<i>Institute</i>	<i>104</i>
<i>NGEE-Artic</i>	<i>111</i>
<i>Scientific Focus Areas (SFA)</i>	<i>129</i>
<i>Student Abstracts</i>	<i>155</i>
<i>TES Lab Research</i>	<i>160</i>
<i>University-Led Research</i>	<i>165</i>
<i>EMSL Poster Abstracts</i>	<i>206</i>
<i>Other Poster Abstracts</i>	<i>209</i>
<i>Appendix I: Abstract Poster Session Assignments</i>	<i>214</i>
<i>Contacts</i>	<i>214</i>

Agenda



**TES/SBR Joint Principal Investigators Meeting
May 5-7, 2014
Bolger Center, Potomac, MD**



Monday, May 5, 2014

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

Tuesday, May 6, 2014

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)** **Bayer**

8:00-8:05am Welcome and Introductory Comments.....P. Bayer

8:05-8:20am BER Programs.....S. Weatherwax

8:20-8:35am CESD Programs & Strategic Directions.....G. Gernaert

8:35-8:55am Accelerated Climate Model for Energy (ACME).....D. Koch

8:55-9:15am CESD Data/Modeling Efforts.....J. Hnilo

9:15-9:35am TES Program Goals, Objectives, Program Structure and Highlights.....D. Stover

9:35-9:55am SBR Program Goals, Objectives, Program Structure and Highlights.....D. Lesmes

9:55-10:15am **Break**

10:15-12:15pm **Plenary Session I – Mechanistic Modeling of Terrestrial Environments: “Bedrock to Atmosphere” (Ben Franklin Hall)** **Lesmes**

10:15-10:45am The GEWaSC Framework: A Genome-Enabled Approach to MultiScale Modeling of Complex Microbial, Biogeochemical and Hydrological Processes..... C. Steefel, E. Brodie

- 10:45-11:15am NGEE-Arctic: Migrating Knowledge across Scales to Improve Climate Prediction.....P. Thornton
- 11:15-11:45am Diagnosing Scaling Behavior of Groundwater with a Fully-Integrated, High Resolution Hydrologic Model Simulated over the Continental US: Watersheds to Continents.....R. Maxwell
- 11:45-12:15pm Multiscale Modeling of Land-Atmosphere Interactions in CESM.....S. Denning
- 12:15-2:00pm **Lunch (Osgood Building)**
- 12:30-2:00pm Working Group Sessions (“To Go” Lunches)
- Hg Working Group (Room 17).....T. Barkay, S. Brooks, N.Yee
- Rads Working Group (Room 18/19).....S. Fendorf, N. Hess, B. Powell
- 2:00-5:00pm **Poster Session I (Franklin Building: Rooms 1, 20, 21, and 23)**
- 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: SPRUCE (Ben Franklin Hall)* **Stover**
- 7:00-7:20pm The S1 Bog Carbon Cycle and Projected Warming Responses for the SPRUCE Experiment.....P. Hanson
- 7:20-7:40pm Coupling Peat Decomposition and Metagenomics to Incorporate Molecular Scale Processes into Climate Models.....J. Kostka
- 7:40-8:00pm Do all 'Bogs' have Similar Anaerobic Carbon Dynamics and Microbial Community Structure? Putting the SPRUCE Site in a Regional Perspective.....S. Bridgman
- 8:00-8:20pm Organic N cycling at SPRUCE.....K. Hofmockel
- 8:20pm Discussion
- 8:30pm Adjourn
- Concurrent Session 2: Science Advances Enabled by EMSL Capabilities (Room 3)* **Bayer/Hess**

- 7:00-7:10pm An Overview of EMSL Science and an Example from Recent Structural Studies of the Major Pilin Protein from *Geobacter sulfurreducens*K. Mueller
- 7:10-7:20pm High-Resolution Molecular Profiling of Permafrost Soil Organic Carbon Composition and Degradation.....B. Gu
- 7:20-7:30pm Multi-System Analysis of Microbial Biofilms.....M. Marshall
- 7:30-7:40pm Pore-Scale and Continuum Simulation of Microfluidics Experiments on Reactive Transport and Multiphase Flow Conducted at EMSL.....A. Valocchi
- 7:40-7:50pm X-ray Tomographic Imaging of Hydraulic Modeling of Plant Roots.....C. Liu
- 7:50-8:00pm Connecting Soil Organic Matter (SOM) Residence Time with SOM Molecular Structure and the Soil Environment.....M. Torn
- 8:00-8:10pm Integrated Soil Organic C Analyses at EMSL Enable New Understanding of Soil C Protection Mechanisms.....V. Bailey
- 8:10-8:20pm Uranium Immobilization in an Iron- and Organic Matter-Rich Rhizosphere of a Native Wetland Plant.....D. Kaplan
- 8:20pm Discussion
- 8:30pm Adjourn

Concurrent Session 3: Inorganic Biogeochemistry (Room 17)

Lesmes

- 7:00-7:20pm Electron Transfer and Atom Exchange Between Fe(II) and Structural Fe(III) in Clays.....M. Scherer
- 7:20-7:40pm Reactivity of Iron-Bearing Phyllosilicates with Uranium and Chromium Through Redox Transition Zones.....B. Burgos
- 7:40-8:00pm Dominant Mechanisms of Uranium-Phosphate Reactions in Subsurface Sediments.....J. Catalano
- 8:00-8:20pm Scaling of Molecular Processes to Quantify Biogeochemical Reaction and Transport of Uranium in Subsurface Systems.....P. O'Day
- 8:20pm Discussion
- 8:30pm Adjourn

Concurrent Session 4: Hydrobiogeochemistry (Room 18/19)

Hirsch/Kuperberg

- 7:00-7:20pm Methane Oxidation in Boreal Peatlands: A Joint Field, Laboratory and Modeling Investigation.....R. Neumann
- 7:20-7:40pm Microbial Dynamics in Arctic Tundra Soils: The Interplay of Plants, Soils, and Extreme Climate.....M. Wallenstein
- 7:40-8:00pm Strikingly Different Form of Organic Carbon in Soils of Temperate and Permafrost Soils: Implications for Carbon and Metal Cycling.....S. Myneni
- 8:00-8:20pm Fate of Uranium During Transport Across the Groundwater-Surface Water Interface.....P. Jaffe
- 8:20pm Discussion
- 8:30pm Adjourn

Wednesday, May 7, 2014

- 6:30-8:00am **Breakfast (Osgood Building)**
- 8:00-9:00am **Plenary Session II (Ben Franklin Hall)** **Hirsch**
- 8:00-8:30am Model-Data Synthesis of Ecosystem Responses to Elevated CO₂: From Deserts to Temperate Forests of the U.S.....A. Walker
- 8:30-9:00am Integrating Microbial Ecology with Hydro-Biogeochemistry.....J. Stegen
- 9:00-12:00pm **Poster Session II (Franklin Building: Rooms 1, 20, 21, and 23)**
- 9:00-10:30am Poster Subsession C
- 10:30-12:00pm Poster Subsession D
- 12:00-1:30pm **Lunch (Osgood Building)**
- 1:30-3:00pm **Plenary Session III –Plant Genomics to Ecosystem Function (Ben Franklin Hall)** **Lesmes**
- 1:30-2:00pm The Challenges and Opportunities for Extending Plant Genomics to Climate Research and Modeling.....D. Weston
- 2:00-2:30pm Hydraulic Redistribution of Water through Plant Roots - Implications for Carbon Cycling and Energy Flux at Multiple Scales.....Z. Cardon
- 2:30-3:00pm Multiscale Modeling of Ecosystem Structure and Function.....G. Katul
- 3:00-4:30pm **Concurrent Sessions – II (Franklin Building)**

Concurrent Session 5: Disturbances and Responses in Terrestrial Ecosystems (Ben Franklin Hall)

Stover

- 3:00-3:20pm B4WarmED: Warming X Rainfall Manipulation Shifts Integrated Soil and Plant Community Processes in a Boreal Ecotone Experiment.....P. Reich
- 3:20-3:40pm Carbon and Energy Balance Consequences of Widespread Mortality in Pinon-Juniper Woodlands.....M. Litvak
- 3:40-4:00pm Resistance and Resilience of a Grassland Ecosystem to Climate Extremes.....M. Smith
- 4:00-4:20pm Deconvolving Local Versus Regional Controls over Plant and Ecosystem Responses to Climate Change in Pacific Northwest Prairies.....L. Pfeifer-Meister
- 4:20pm Discussion
- 4:30pm Adjourn

Concurrent Session 6: Arctic (Room 4)

Kuperberg

- 3:00-3:20pm Geophysical Evidence for Surface-Subsurface Interactions in Arctic Tundra.....S. Hubbard
- 3:20-3:40pm Geomorphological Controls on Water and Terrestrial Ecosystem Processes within Ice-Rich Polygonal Landscapes.....C. Wilson
- 3:40-4:00pm Multi-Disciplinary Research Targets Improved Representation of Arctic Ecosystems in Earth System Models.....D. Graham
- 4:00-4:20pm The Impact of Permafrost Carbon Loss on the Carbon Balance of an Experimentally Warmed Tundra Ecosystem.....T. Schuur
- 4:20pm Discussion
- 4:30pm Adjourn

Concurrent Session 7: Environmental Microbiology (Room 3)

Bayer

- 3:00-3:20pm Diversity and Metabolic Potential of the Terrestrial Subsurface Microbiome and its Influence on Biogeochemical Cycling.....J. Banfield
- 3:20-3:40pm Omics and Geochemistry: the ENIGMA 100-Well Survey.....T. Hazen
- 3:40-4:00pm Hg(0) Oxidation by Anaerobic Bacteria.....N. Yee

4:00-4:20pm Sulfur-Mediated Electron Shuttling during Bacterial Iron Reduction.....T. Flynn

4:20pm Discussion

4:30pm Adjourn

Breakout Session 8: "Building Better Modeling Tools for Practitioners" (Room 18/19) **Lesmes**

3:00-3:15pm Experiment-Inspired Software Design and Ecosystem Modular Testing for CLM DevelopmentD. Wang

3:15-3:30pm Expanding the Role of Reactive Transport Modeling within the Biogeochemical Sciences.....L. Li

3:30-3:45pm Lightning Talks.....Multiple Presenters

3:45-4:30pm Discussion

4:30pm Adjourn

4:30-5:30pm **Plenary Session IV – How Science Informs Policy (Ben Franklin Hall)** **Kuperberg**

4:30-4:45pm Science & Policy – An Investment Perspective.....J. Bucknall, World Bank

4:45-5:00pm Science & Policy – A Diplomatic Perspective.....D. Reidmiller, U.S. Dept of State

5:00-5:15pm Science & Policy – A Research Funding Perspective.....K. Barrett, NOAA

5:15-5:30pm Science & Policy – A Scientific Perspective.....P. Duffy, USGCRP

5:30-5:45pm **Closeout/Announcements**

5:45-7:00pm **Dinner (Osgood Building)**

7:00pm **Adjourn**

7:00-8:30pm **Team Meetings (Franklin Building)**

Team Meetings

NGEE-Arctic (Ben Franklin Hall).....S. Wullschleger

SPRUCO (Classroom 18/19).....P. Hanson

Presentation Abstracts

The GEWaSC Framework: A Genome-Enabled Approach to MultiScale Modeling of Coupled Microbial Biogeochemical and Hydrological Processes

Carl Steefel (CISTeefel@lbl.gov) - Lawrence Berkeley National Lab (PI), E.L. Brodie, S.B. Yabusaki, E. King, N. Bouskill, S. Molins B. Arora, U. Karoz, N. Spycher, R.M. Maxwell, A. Navarre-Sitchler, J. Beisman; Project Leader: Susan Hubbard; (Co-PIs).

In order to improve our ability to predict the effect of climate change on carbon and nutrient cycling, we are developing a genome-enabled multiscale reactive transport framework (GEWaSC) that couples microbial composition, competition, and activity to biogeochemical processes and the hydrologic cycle at the watershed scale. This new simulation capability goes beyond conventional watershed models by ultimately integrating surface processes (e.g., those taking place in the soil and surface waters) with the subsurface flow and transport in a formal manner to provide a complete description of the biogeochemistry of carbon and nutrient cycles within a catchment. A novel feature of the modeling approach is the coupling of microbial functional groups (guilds) inferred from trait-based models, parameterized using site-specific 'omic data, with a comprehensive simulation of the biogeochemical network. The composition of these guilds is a function of the organisms' physiological traits along with environmental, physical and geochemical conditions that exist across flow paths to create 'hot spots' of activity. Our approach models the rate of nutrient uptake and the thermodynamics of coupled electron donors and acceptors to predict the energy available for respiration, biomass development and exo-enzyme production. Each group within a functional guild is parameterized with a unique combination of traits governing organism fitness under dynamic environmental conditions.

Initial model application is to biogeochemical and microbial dynamics within the Rifle Flood Plain system, a component of the greater Colorado River system. Preliminary work focuses on carbon and nitrogen cycling at the Rifle Flood Plain site and is being carried out at four scales: 1) development of microbial trait-based (EcoTrait) simulation capabilities based on genomic studies and designed for integration with flow and transport models, 2) 1D and 2D simulations along a transect through the Rifle Flood Plain with both vadose zone and groundwater contributions, 3) 3D simulations of the Rifle Flood Plain focusing on seasonal oxygen consumption in upstream and Naturally Reduced Zones (NRZ), and 4) simulations of the greater Rifle watershed, with a focus on the contribution of upland groundwater fluxes and the role of heterogeneities in establishing the sub-oxic status of the aquifer. Initial modeling and data analysis emphasize the important role of the NRZ (or "biogeochemical hotspots") in mediating the redox status of the alluvial plain aquifer, with the important role of microbially-mediated carbon and sulfur oxidation indicated by elevated fluxes of inorganic carbon and isotope ratios of groundwater sulfide.

NGEE-Arctic: Migrating Knowledge Across Scales to Improve Climate Prediction

Peter Thornton (thorntonpe@ornl.gov) - Oak Ridge National Laboratory, Stan Wullschleger (PI).

Observations, experimentation, and modeling are being conducted across a range of scales in a permafrost tundra ecosystem in an effort to improve process-level understanding of physical, biogeochemical, biological, and ecological dynamics and interactions, with the goal of migrating this new knowledge up in scale to improve climate prediction. Models are being constructed and exercised in a nested hierarchical framework, with very fine-scale process-resolving models being parameterized using multiple observational constraints, and being run over selected sub-regions to inform coarser-scale parameterizations. Observations and laboratory studies in several process domains and across multiple spatial and temporal scales are being used to inform parameterizations, while independent observations and laboratory manipulations are being carried out to evaluate models and quantify model prediction uncertainties. Some of the developments presented here are being targeted for migration to new global-scale climate prediction frameworks. Successful generation of new process-level knowledge and migration of knowledge into predictive modeling frameworks depends on a rapid, accurate, and understandable approach to managing multi-faceted data. The project has developed and is using an integrated approach to collection, sharing, and management of observational, experimental, and modeling data.

Diagnosing Scaling Behavior of Groundwater with a Fully-Integrated, High Resolution Hydrologic Model Simulated over the Continental US: Watersheds to Continents

Reed Maxwell (rmaxwell@mines.edu) - Colorado School of Mines.

Groundwater is an important component of the hydrologic cycle yet its importance is often overlooked. Aquifers are a critical water resource, particularly in irrigation, but also participates in moderating the land-energy balance over the so-called critical zone of 2-10m in water table depth. Yet, the scaling behavior of groundwater is not well known. Here, we present the results of a fully-integrated hydrologic model run over a 6.3M km² domain that covers much of North America focused on the continental United States. This model encompasses both the Mississippi and Colorado River watersheds in their entirety at 1km resolution and is constructed using the fully-integrated groundwater-vadose zone-surface water-land surface model, ParFlow. Results from this work are compared to observations (both of surface water flow and groundwater depths) and approaches are presented for observing of these integrated systems. Furthermore, results are used to understand the scaling behavior of groundwater over the continent at high resolution. Implications for understanding dominant hydrological processes at large scales will be discussed.

Multiscale Modeling of Land-Atmosphere Interactions in CESM

Scott Denning (scott.denning@colostate.edu) - Colorado State University (PI).

Interactions between the vegetated land and the atmosphere occur at spatial scales that are orders of magnitude too small to resolve in global climate models. Unfortunately some of these processes are not linear, meaning that the response to the average forcing can be dramatically different than the average response to the forcing. Common examples are the saturation of the photosynthetic light response or the threshold for drought stress in response to changes in root zone soil moisture. Traditional land surface parameterization uses several coexisting “tiles” to represent heterogeneous vegetation and soils, but all tiles in a given climate model grid cell share the same precipitation, radiation, humidity, etc.

The S1-Bog Carbon Cycle and Projected Warming Responses for the SPRUCE Experiment

Paul Hanson (hansonpj@ornl.gov) - Oak Ridge National Laboratory (PI), Daniel M. Ricciuto, ORNL; Colleen M. Iversen, ORNL; Natalie A. Griffiths, ORNL; Stephen D. Sebestyen, USDAFS; Anna Jensen, ORNL; Jeffrey M. Warren, ORNL; Richard J. Norby, ORNL; Xiaoying Shi, ORNL; Xiaofeng Xu, ORNL; Karis J. McFarlane, LLNL (Co-PIs).

The S1-Bog is a Picea-Sphagnum peatland located on the Marcell Experimental Forest in northern Minnesota that is being characterized and prepared for experimental manipulations to evaluate organismal and ecosystem carbon cycle responses to warming and elevated CO₂. These saturated wetlands are characterized by deep histosol soils (2-3 meters). S1-Bog belowground C stocks equal 2200 MgC ha⁻¹. Similar ecosystems occupy ~1 percent of global ice-free land area, but contain 300 to 700 Pg of global soil C (atmospheric C = 589 Pg C).

Calibrated peat ages and carbon stocks below -40 cm (1500 to 12000 yBP) show a post-glacial, millennial C accumulation rate of 21 gC m⁻² y⁻¹ for stable peat with a C:N ratio around 20. In the surface peat (-40 to 0 cm) C:N ratios rise to values near 50 reflecting freshly deposited plant material (Sphagnum and various woody species). Net ecosystem production within the bog ranges from 100 to 300 gC m⁻² y⁻¹ and is considerably higher than the millennial accumulation rate. Labile carbon losses during surface aerobic decomposition account for the difference. The SPRUCE experiment is designed to provide data on the susceptibility of both the current C cycle and millennial carbon stocks to potential future warming. Detailed characterization of biogeochemical cycles for limiting elements with the bog (N, P, Ca, Mg, etc) will be conducted to characterize mineralization rates of such elements from accumulated peat. Mineralization may effectively fertilize the bog vegetation and compensate for decomposition losses through enhancement of annual production.

Models are being structured to better represent bog biogeochemistry and hydrology. ORNL efforts are focused on extending the Community Land Model (CLM) version 4.5 for the S1-Bog and vegetated wetland systems in general. Initial simulations use a 2-column structure to represent hummock-hollow topography with lateral flows and vertically resolved soil carbon and nitrogen. CLM4.5 is also being updated to include a microbial decomposition model, which is producing more realistic predictions of observed pre-treatment CO₂ and CH₄ fluxes. Model simulations with warming suggest a substantial drop in water table. Initial hypotheses suggest that peat and C accumulation may be sustained for low levels of warming, but shift to a pattern of net carbon release in the forms of CO₂ and CH₄ for greater levels of warming. Model projections for various processes will be discussed in the context of planned warming manipulations: belowground-only (2014) and whole-ecosystem (2015 and beyond).

Coupling Peat Decomposition and Metagenomics to Incorporate Molecular Scale Processes into Climate Models

Joel Kostka (joel.kostka@biology.gatech.edu) - Georgia Institute of Technology, Joel E. Kostka (PI), Jeff Chanton, FSU; Bill Cooper, FSU; Chris Schadt, ORNL (Co-PIs).

The goal of this project is to investigate changes in the structure of dissolved and solid phase organic matter, the production of CO₂ and CH₄, and the composition of decomposer microbial communities in response to the climatic forcing of environmental processes that determine the balance between carbon gas production versus storage and sequestration in peatlands. Cutting-edge analytical chemistry and next generation sequencing of microbial genes has been applied to habitats at the Marcell Experimental Forest (MEF), where the US DOE's Oak Ridge National Laboratory and the USDA Forest Service are constructing a large-scale ecosystem study entitled, "Spruce and Peatland Responses Under Climatic and Environmental Change" (SPRUCE). Our study represents a comprehensive characterization of the sources, transformation, and decomposition of organic matter in the S1 bog at MEF. Multiple lines of evidence point to distinct, vertical zones of organic matter transformation: 1) the acrotelm consisting of living mosses, root material, and newly formed litter (0-30 cm), 2) the mesotelm, a mid-depth transition zone (30-75 cm) characterized by labile organic C compounds and intense decomposition, and 3) the underlying catotelm (below 75cm) characterized by refractory organic compounds as well as relatively low decomposition rates. These zones are in part defined by physical changes in hydraulic conductivity and water table depth. O-alkyl-C, which represents the carbohydrate fraction in the peat, was shown to be an excellent proxy for soil decomposition rates. The carbon cycle in deep peat was shown to be fueled by modern carbon sources further indicating that hydrology and surface vegetation play a role in belowground carbon cycling. We provide the first metagenomic study of an ombrotrophic peat bog, with novel insights into microbial specialization and functions in this unique terrestrial ecosystem. Vertical structuring of microbial communities closely paralleled the chemical evolution of peat, with large shifts in microbial populations occurring in the biogeochemical hotspot, the mesotelm, where the highest rates of decomposition were detected. Stable isotope geochemistry and potential rates of methane production paralleled vertical changes in methanogen community composition to indicate a predominance of acetoclastic methanogenesis mediated by the Methanosarcinales in the mesotelm, while hydrogen-utilizing methanogens dominated in the deeper catotelm. Preliminary evidence suggests that the availability of phosphorus limits the microbially-mediated turnover of organic carbon at MEF. Prior to initiation of the experimental treatments, our study provides key baseline data for the SPRUCE site on the vertical stratification of peat decomposition, key enzymatic pathways, and key enzymatic pathways.

Do all 'Bogs' have Similar Anaerobic Carbon Dynamics and Microbial Community Structure? Putting the SPRUCE Site in a Regional Perspective

Scott Bridgham (bridgham@uoregon.edu) - University of Oregon (PI), co-PIs: Jeffrey P. Chanton, Florida State University; Jason K. Keller, Chapman University; Joel E. Kostka, Georgia Institute of Technology; Postdoc Authors: Xueju Lin, Georgia Institute of Technology; Cassandra A. Medvedeff, Chapman University; Laurel Pfeifer-Meister, University of Oregon; Malak M. Tfaily, Pacific Northwest National Laboratory.

The S1 peatland in Minnesota where the SPRUCE experiment is located has typically been described as an ombrotrophic (i.e., rain-fed) bog, but recent evidence suggests that it is weakly minerotrophic (i.e., occasional ground-water inputs into surface peat layers). It also has extensive hummock/hollow development. We compared seasonal CH₄ fluxes, anaerobic C cycling, and microbial gene and transcript abundance in S1 to a nearby poor fen (Bog Lake Fen [BLF]) and to a true ombrotrophic bog (Zim) to examine to what degree S1 represents regional Sphagnum-moss dominated, low pH peatlands. Zim differs from S1 in being primarily covered by Sphagnum hummocks, whereas BLF is primarily covered by a Sphagnum and graminoid lawn.

CH₄ emissions were high in S1 and BLF but very low in Zim, with isotopic data suggesting extensive CH₄ oxidation in Zim. In situ rates of CH₄ production in July 2013 were relatively high in surface peat in S1 hollows and BLF but decreased dramatically with depth. Rates in Zim and S1 hummocks were low throughout the peat profile, partially reflecting for Zim lower soil temperatures. Production potentials over 153 days at 18°C showed Zim peat to have a longer (~ 1 month) lag period before substantial CH₄ production compared to the other sites. All peats had very low CH₄ production potentials in deeper peat. In situ porewater CH₄ concentration profiles were similar for all sites. Isotopic data suggested that the acetoclastic CH₄ pathway was most important in surface BLF peat and the H₂/CO₂ pathway was dominant throughout the peat profile in S1 and Zim. Chemical characterization of DOM and solid peat generally indicated that S1 and Zim were similar at a particular depth and could not explain differences in CH₄ production potentials.

There were no differences in *mcrA* gene or transcript abundance among sites, but the *mcrA* transcript-to-gene ratio was highest in S1, in concordance with its high CH₄ production potential. Surface peat *pmoA* gene and transcript abundances were much higher in Zim and BLF compared to S1, and the transcript-to-gene ratio was highest in Zim, supporting an interpretation of high CH₄ oxidation at that site.

Our results indicate substantial differences in CH₄ emissions, anaerobic C cycling dynamics, and microbial functionality in these three peatlands despite them all having low pH and being covered by Sphagnum mosses. S1 appears to be intermediate in many ways between true ombrotrophic bogs and poor fens, reflecting its weakly minerotrophic status.

Organic N Cycling at SPRUCE

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At the heart of microbial C-N cycling are microbial metabolism and extracellular enzymes. Amino acid release by microbial extracellular proteases is important for N turnover and the production of bioavailable N in forest soils. Amino acid production is particularly important in boreal systems, where N supply strongly influences both decomposition and plant primary productivity. Yet little is known about the abundance, potential activity, or diversity of the microbial extracellular protease encoding genes in peatland forests. To evaluate the overall enzymatic potential for decomposition we measured microbial biomass and extracellular enzyme activity at three depths (+10 cm, 0 cm and -10 cm relative to peat hollows) at the Spruce and Peatland Responses Under Climatic and Environmental Change (SPRUCE) experiment site in the Marcell National Forest, Minnesota, USA. Samples were collected from fresh peat in June and September 2013. In addition, fungal ingrowth cores filled with sterilized peat were incubated in situ from June to September to assess new microbial inputs. In both fresh peat and ingrowth cores enzymatic potential diminished with peat depth. Potential enzyme activity was lower and stratification of activity by depth was more pronounced in fungal ingrowth cores compared to native peat cores. Proteolytic microorganisms present in the SPRUCE bog were characterized by concurrent analysis of metagenomic data from 0-10 cm peat samples from February 2012. Microbial protease genes were abundant and diverse, with a total of 32,533 microbial extracellular protease genes in nine extracellular protease gene groups. Among identified proteases, sequences encoding for the enzymes aminopeptidase and trypsin were the most prevalent in all samples. The majority of genes resembled known proteases of bacterial origin, primarily of the Proteobacteria, Acidobacteria and Actinobacteria. Less abundant were fungal protease genes, which were predominantly from the Ascomycota, and Archeal protease genes most similar to Crenarchaeota origin. While both fungal and bacterial genes consistently diminish with depth, archaeal RNA polymerase and extracellular protease genes were more abundant at 25-75 cm than 0-10 cm. Our results indicate that peatland systems have a stratified microbial extracellular protease potential across depth. Although fungi are commonly considered to be central regulators of proteolysis, our analysis suggests that bacteria may be very important at the surface and archaea deeper in the profile. The low importance of fungal proteolysis, particularly at depth, presumably limits vertical nitrogen translocation via fungal hyphae and contributes to the long-term storage of N (and C) in unavailable pools below the aerobic zone.

An Overview of EMSL Science and an Example from Recent Structural Studies of the Major Pilin Protein from *Geobacter Sulfurreducens*

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EMSL, a DOE national user facility in Richland WA, provides integrated experimental and computational resources and expertise for scientific research and discovery, generating foundational scientific knowledge needed to address climate, bioenergy, and environmental challenges of importance to BER, DOE, and the nation. EMSL users and staff address science gaps that limit the translation of fundamental molecular-scale science into solutions for DOE's most pressing challenges.

Through the integration of field, experimental, and computational approaches, EMSL users gain new knowledge of molecular-scale phenomena that can be parameterized and integrated into the types of local, regional, and global scale models designed to predict the impact of life on earth's climate and environment. To enhance EMSL's scientific impact and unique capabilities, user proposal calls focus on four BER- and DOE-aligned science themes in atmospheric aerosol chemistry, biosystems dynamics and design, terrestrial and subsurface ecosystems, and energy materials and processes. EMSL is also active in leveraging its capabilities with other DOE user facilities to provide maximal scientific advantage to DOE and the scientific community. As an example, EMSL and the DOE Joint Genome Institute (JGI) have recently sponsored joint user calls to take best advantage of DOE's genomic/transcriptomic and other bio-omic capabilities for systems biology advances.

As an example of current research carried out at EMSL and of interest to researchers in the SBR and TES programs, we have recently determined the atomic resolution structure in detergent micelles of the major pilin protein from *Geobacter sulfurreducens*, PilA, using high resolution NMR spectroscopy. *Geobacter sulfurreducens* and related species of proteobacteria can utilize a wide range of insoluble extracellular electron acceptors, such as metal oxides, during respiration; and the transport of electrons by *G. sulfurreducens* is thought to be facilitated by filamentous type IV pili, often referred to as bacterial nanowires. We have determined that the PilA protein is greater than 85% α -helical and is structurally similar to the N-terminal region of other non-conductive type IVa pilins. Modeling of the PilA NMR structure onto the type IVa pilus fiber model from *Neisseria gonorrhoeae* provides insight into the organization of aromatic amino acids that have been suggested to play a role in electrical conduction.

High-Resolution Molecular Profiling of Permafrost Soil Organic Carbon Composition and Degradation

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Microbial degradation of soil organic matter (SOM) is a key process for terrestrial carbon (C) cycling, though the dynamics of these transformations remain unclear at the molecular level. As part of the Next Generation Ecosystem Experiment (NGEE-Arctic) research, this study reports the application of ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) to profile molecular components of Arctic SOM collected from the surface water and the mineral horizon of a low-centered polygon soil at Barrow Environmental Observatory (BEO) (Barrow, AK). Soil samples were subjected to anaerobic warming experiments for a period of 40 days, and the SOM was extracted with water and 0.1 M NaOH and analyzed before and after the incubation to determine the components of organic C that were degraded over the course of the study. A CHO index based on molecular composition data was utilized to codify SOM components according to their observed degradation potential. Carbohydrate- and lignin-like compounds in the water-soluble fraction (WSF) demonstrated a high degradation potential, while structures with similar stoichiometries in the base-soluble fraction (BSF) were not readily degraded. The WSF of SOM also shifted to a wider range of measured molecular masses including an increased prevalence of larger compounds, while the size distribution of compounds in the BSF changed little over the same period. Additionally, the molecular profiling data indicated an apparently ordered incorporation of organic nitrogen in the BSF immobilized as primary and secondary amines, possibly as components of N-heterocycles, which may provide insight into nitrogen immobilization or mobilization processes in SOM. Our study represents an important technical advancement for studying Arctic SOM with improved understanding of the detailed molecular properties of soil organic C and, ultimately, the ability to accurately represent SOM in climate models that will predict the impact of climate change on soil C and nutrient cycling.

Multi-system Analysis of Microbial Biofilms

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The majority of microorganisms in natural and engineered environments live in structured communities such as biofilms. Biofilms are comprised of microbial cells and a poorly characterized organic matrix commonly referred to as extracellular polymeric substance (EPS) that may support microbial interactions and biogeochemical reactions including extracellular electron transfer. Using high-resolution electron microscopy (EM) imaging, we have shown copious amounts of highly hydrated bacterial EPS are produced during microbial metal reduction. The co-location of extracellular electron transfer proteins and nanoparticulate reduced metal suggested that EPS played a key role in metal capture and precipitation.

Here we present a multi-faceted approach to determine the composition of biofilm EPS using synchrotron-based X-ray and infrared (IR) microimaging techniques combined with mass spectrometry imaging and high-resolution EM at the Environmental Molecular Sciences Laboratory. The result is a spatially resolved, complex chemical imaging of a biofilm community. X-ray microtomography produced images of hydrated biofilms to reveal the complex microstructure within a biofilm. Contrasting agents enhanced biofilm visibility at the high energies used. To investigate the micrometer- to nanometer-scale chemical signatures of biofilms, a cryo-sample preparation technique produced ultrathin biofilm sections for scanning transmission x-ray microscopy (STXM) and synchrotron IR microimaging. In STXM studies, we mapped the unique carbon signatures of biological molecules and found distinct differences between the cell surface and the EPS matrix. Concurrent with these studies, we used IR microimaging to produce high-megapixel datasets with IR spectral data showing the locations of key biofilm components (i.e., proteins, sugars, flavins, nucleic acids, lipids). The spatially resolved IR results were corroborated with bulk IR chemical data using chemically fractionated regions of biofilms.

In situ imaging was conducted using a novel microfluidic reactor for biofilm growth, confocal laser scanning microscopy analysis, and hydrated-state, time-of-flight secondary ion mass spectrometry imaging. We generated high-resolution two-dimensional chemical images of biofilms at their surface attachment interface and detected characteristic fatty acid fragments from microfluidic reactor-grown biofilms. These fatty acid fragments are being investigated as key factors for how biofilms attach to a surface in a microfluidic reactor.

The integration of the multiscale structural studies and in situ imaging of hydrated biofilms 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.

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Pore-Scale and Continuum Simulation of Microfluidics Experiments on Reactive Transport and Multiphase Flow conducted at EMSL

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Advances in microfabrication and imaging technology have enabled direct observation of coupled flow and reaction process at the pore scale. A state-of-art user facility was developed at EMSL to enable direct application of these advances to the study of pore scale processes in groundwater and deep subsurface reservoirs. Similar advances in computing power and numerical methods allow for direct numerical simulation of pore-scale processes from first-principles without any adjustable parameters. Investigators at the University of Illinois have been collaborating with EMSL scientists to conduct pore-scale experiments and simulations to investigate a variety of processes, including mixing-controlled aqueous reactions, mixing-controlled precipitation, and multi-phase flow. These processes are important to understand for many science and engineering questions, including contaminant fate and transport, biogeochemical dynamics in the root zone, and geological sequestration of carbon dioxide. By combining pore-scale simulation and experiments we have studied the impact of pore geometry and flow rate on mixing, how mixing and solution composition affects precipitate mineralogy, stability, and pore blocking, and the impact of flow rate and pore geometry on two-phase saturation and interfacial area. Numerical modeling allows testing of hypotheses about fundamental reaction mechanisms provides a tool for upscaling.

X-ray Tomographic Imaging and Hydraulic Modeling of Plant Roots

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This presentation will describe a study of imaging a plant root system, simulating three dimensional water flow inside roots in interactions with surrounding soils, and assessing how root hydraulic process affects soil hydrological properties under unsaturated conditions. A 3-D structure of a plant root was imaged using an X-ray tomography facility (X-Tek/Metris XTH 320/225 kV system) at Environmental Molecular Science Laboratory (EMSL), a BER facility located at PNNL. The data were collected at 85 kV and 190 A x-ray power for optimum image quality and contrast. The sample was rotated continuously during the scan with momentary stops to collect each projection (shuttling mode) to minimize ring artifacts. 3142 projections were collected over 360 degrees with 1 second exposure time and 4 frames per projection. Image voxel size was 31x31x31 microns. The raw images were reconstructed to get a three-dimensional dataset to produce a volume file of approximately 1500x1500x1000 voxels in dimension. The reconstructed volume file was used to create a stack of images, which were further processed to segregate the root from the surrounding soil. The 3-D images of the root system were then digitized to form 3-D numerical domains of the root and surrounding soils at the voxel resolution. A unified multi-scale model, which merges Navier Stokes equation with Darcy law to form a single set of equations under both saturated and unsaturated conditions, was used to simulate coupled flow inside the roots driven by water demand from the plant canopy. Day and night change of water demand from the canopy was used as external force in the simulation for water flow inside and outside of the plant roots. The high density simulation results were then used to evaluate the effective parameterization of unsaturated flow, and to assess the importance of root hydraulic flow in simulating water migration in soils.

Connecting Soil Organic Matter (SOM) Residence Time with SOM Molecular Structure and the Soil Environment

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Soil organic matter (SOM) dynamics are governed by the interaction of SOM with the soil physical-chemical environment, microbial activity, other biogeochemical cycles, and landscape processes such as erosion and forest-pasture conversion. In this talk we will present highlights from four studies that looked at SOM molecular structure in relation to these ecosystem processes and conditions. We used solid-state CP MAS ^{13}C nuclear magnetic resonance (NMR) spectroscopy to investigate the chemical structure of vegetation tissues, and of soil fractions (particulate organic carbon (free light fraction), intra-aggregate light fraction, and mineral-associated fraction). This was combined with radiocarbon analysis to estimate SOM pool sizes, chemical quality, and turnover times - on soils collected from long term experiments or environmental gradients. The NMR analysis was done at the DOE Environmental Molecular Sciences Laboratory (EMSL) at PNNL, whose scientists also assisted with the interpretation. The four highlights to be presented concern (1) nitrogen cycling: process-level links between microbial responses to N deposition and shifts in soil organic matter (SOM) quality and quantity. (2) Erosion and Deposition: the influence of the physico-chemical state (i.e., in aggregates, mineral-associated) and molecular structure of OM on its storage and persistence in different types of eroding and depositional landform positions. (3) pasture-forest transitions: changes in SOM cycling with time in tropical secondary forests regrowing on abandoned pastures. (4) influence of chemistry of plant inputs: soil carbon dynamics in adjacent old-growth redwood forest and prairie, with contrasting tissue lifespan and litter chemistry.

Integrated Soil Organic C Analyses at EMSL Enable New Understanding of Soil C Protection Mechanisms

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Our conceptual understanding of the soil C cycle is largely based on chemical or physical separations of operationally defined soil C pools. This representation has provided a rich foundation of gross C transformations and rates. However, new technical advances in spatially-resolved sampling and high-resolution mass spectrometry can now be applied to soil samples to reveal new spatial and chemical detail about the arrangement and molecular nature of native soil organic C. Laser-ablation-aerosol mass spectrometry (LA-AMS) has been used to “map” C:N ratios in sub-millimeter soil aggregates, and to characterize the chemical nature of soil C in unstructured soil samples. Fourier transform ion cyclotron resonance (FTICR) mass spectrometry can identify more than 1500 different peaks in the C profile of pore water samples or associated with soil solids. Molecular formula assigned to these peaks allows differentiation into chemical compound classes such as lipids, proteins, unsaturated hydrocarbons, lignins, carbohydrates, amino sugars, tannins, and condensed hydrocarbons. Integrating these techniques and data will yield exciting new insights into the balance between physical protection and chemical recalcitrance as mechanisms controlling the persistence of SOC in soils. A clear characterization of this balance will also lead to an improved understanding of how ecosystem perturbations lead to increased losses of SOC and net greenhouse gas emissions.

Uranium Immobilization in an Iron- and Organic Matter-Rich Rhizosphere of a Native Wetland Plant

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Discharge of contaminated groundwater to surface waters is of concern at many DOE facilities. It is at this interface where contaminants come into contact with the biosphere. These wetlands exist in humid as well as arid regions. Furthermore, the numerous sharp biogeochemical transitions occurring in wetlands have profound effects on the ultimate fate of redox-sensitive trace metals and radionuclides, including uranium. The hypothesis of this study was that iron plaques formed on the roots of most wetland plants and their rhizospheres create environmental conditions favorable for the in-situ immobilization of uranium. Greenhouse microcosm studies were conducted using native plants (*Sparganium americanum*) from a wetland located on the Savannah River Site (SRS), Aiken, SC. Bacterial numbers including *Geobacter* sp., Fe(III), as well as total uranium, were highest on roots, followed by sediments near roots, and lowest in zones without much root influence. Results from the μ -XRF mapping on root surfaces indicated a strong spatial correlation between Fe and U, while the analysis via XANES showed that a significant fraction of uranium was reduced to U(IV), indicating that iron cycling in the rhizosphere also results in uranium reduction and immobilization. Under high iron loading, results indicate that co-precipitation of U(VI) with iron might have been an important U removal process. Depth-discrete diffusion porewater samples are being seasonally collected from a depleted-U contaminated wetland located in Steed's Pond on the SRS. Porewater dissolved U concentration fluxes are consistent with our laboratory findings, indicating that during the growing season when there is more active iron reduction, the dissolved U in the sediment pore water is significantly lower. Characterization of the field sediments was conducted to identify the biogeochemical conditions responsible for the enhanced uranium uptake in the rhizosphere. X-ray computed tomography indicate a highly ordered, albeit thin, layer of minerals adjacent to the roots. Mossbauer spectroscopy identified a significant enrichment of ferrihydrite/lepidocrocite/OM-Fe phases within the rhizosphere sediment, as compared to the iron in the bulk sediment, which was composed primarily of nano-goethite. TEM analyses confirm unique mineralogy and the presence of nano-phases in the rhizosphere. Further characterization of uranium in the sediment rhizosphere is planned.

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

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Fe-bearing clay minerals serve as an important source and sink for electrons in redox reactions in various subsurface geochemical environments. Heterogeneous reactions between aqueous Fe(II) and Fe(III) oxides have been extensively studied, leading to a new conceptual framework which includes electron transfer between Fe(II) and structural Fe(III), bulk electron conduction, and Fe(II)-Fe(III)oxide atom exchange. Reactions of aqueous Fe(II) with clay minerals have received much less attention and are often described in terms of surface reactions including ion exchange, surface complexation, and/or surface precipitation. Our objectives here are to:

1. Determine if electron transfer occurs between sorbed Fe(II) and structural Fe(III) in clays over a range of conditions and clay structures.
2. Evaluate whether Fe atom exchange occurs between aqueous Fe(II) and structural Fe(III) in clays, and natural, clay-rich sediments.

We have investigated Fe electron transfer and atom exchange in clay minerals via selective chemical extractions, Fe isotope experiments and computational molecular modeling. Our findings indicate that structural Fe(III) in two nontronite clay minerals (NAu-1 and NAu-2), as well as a montmorillonite clay mineral (SWy-2) is reduced by aqueous Fe(II) and that electron transfer occurs when Fe(II) is sorbed to either basal planes and edge OH-groups of clay mineral NAu-1. Significant electron transfer occurred from edge OH-group bound Fe(II) at pH 7.5. At pH 4.0 and 6.0, where Fe(II) is sorbed primarily to the basal planes, electron transfer still occurred but to a much lower extent than from edge-bound Fe(II). Interestingly, the greatest extent of reduction was observed in the SWy-2 montmorillonite which contains the lowest % by weight Fe (2.8%). Findings from highly enriched isotope experiments suggest that between 5 and 20% Fe atom exchange is occurring between aqueous Fe(II) and structural Fe in a clay mineral. Experiments with higher precision isotope measurements using the multi-collector ICP-MS at Wisconsin confirm these findings. First principles calculations using a small polaron hopping approach suggest surprisingly fast electron mobility at room temperature in nontronite consistent with temperature dependent Mössbauer data. Electron conductivity of bulk nontronite is predicted to be highest through the octahedral sheet, as opposed to the tetrahedral sheet or from the tetrahedral to the octahedral sheet.

Reactivity of Iron-Bearing Phyllosilicates with Uranium and Chromium Through Redox Transition Zones

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Iron-bearing phyllosilicate minerals help establish the hydrogeological and geochemical conditions of redox transition zones because of their small size, limited hydraulic conductivity and redox buffering capacity. The bioreduction of soluble U(VI) to sparingly soluble U(IV) can promote the reduction of clay-Fe(III) through valence cycling. The reductive precipitation of U(VI) to uraninite was previously reported to occur only after a substantial percentage of clay-Fe(III) had been reduced. Using improved analytical techniques we show that concomitant bioreduction of both U(VI) and clay-Fe(III) by *Shewanella putrefaciens* CN32 can occur. Soluble electron shuttles were previously shown to enhance both the rate and extent of clay-Fe(III) bioreduction. Using extended incubation periods we show that electron shuttles enhance only the rate of reduction (overcoming a kinetic limitation) and not the final extent of reduction (a thermodynamic limitation). The first 20% of clay-Fe(III) in nontronite NAu-2 was relatively “easy” (i.e., rapid) to bioreduce while the next 15% of clay-Fe(III) was “harder” (i.e., kinetically-limited) to bioreduce and the remaining 65% of clay-Fe(III) was effectively biologically un-reducible. In abiotic experiments with NAu-2 and biogenic uraninite, 16.4% of clay-Fe(III) was reduced in the presence of excess uraninite. In abiotic experiments with NAu-2 and AH2DS, 18.5 to 19.1% of clay-Fe(III) was reduced in the presence of excess and variable concentrations of AH2DS. A thermodynamic model based on published values of the non-standard state reduction potentials at pH 7.0 (E'_{H}) showed that the abiotic reactions between NAu-2 and uraninite had attained apparent equilibrium. This model also showed that the abiotic reactions between NAu-2 and AH2DS had attained apparent equilibrium. The final extent of clay-Fe(III) reduction was well correlated to the standard state reduction potential at pH 7.0 (E°_{H}) of all of the reductants used in these experiments (AH2DS, CN32, dithionite, uraninite).

We also examined the reduction of nitrobenzene by CN32 in the presence of montmorillonite SWy-2 (low Fe(III) content) and nontronite NAu-2 (high Fe(III) content). Nitrobenzene and other nitroaromatic compounds (NACs) have been selected for study because their redox properties are well known and they have previously been used as redox probe molecules to examine the reactivity of clay-Fe(II). We found that the abiotic reduction of nitrobenzene became increasingly important as clay-Fe(II) accumulated in the system.

Dominant Mechanisms of Uranium-Phosphate Reactions in Subsurface Sediments

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Phosphate addition is an in situ remediation approach that may enhance the sequestration of uranium without requiring sustained reducing conditions. However, the geochemical factors that determine the dominant immobilization mechanisms upon phosphate addition are insufficiently understood to design efficient remediation strategies or accurately predict U(VI) transport. The overall objective of our project is to determine the dominant mechanisms of U(VI)-phosphate reactions in subsurface environments. Our research approach seeks to determine the U(VI)-phosphate precipitates that form from homogeneous solutions, characterize the effects of phosphate on U(VI) adsorption and precipitation on smectite and iron oxide minerals, and investigate how phosphate affects U(VI) speciation and fate in field sediments.

Our initial studies investigated the products of U(VI)-phosphate reactions in the absence and presence of sorbing mineral phases. In homogeneous systems, autunites form even when other U(VI) phosphates are more thermodynamically stable. In the presence of Ca, U(VI) may also sorb to or coprecipitate with calcium phosphates. In heterogeneous systems, phosphate has no macroscopic effect on U(VI) adsorption to a smectite clay despite LIFS and EXAFS spectra showing a clear change in surface speciation. In contrast, phosphate enhanced U(VI) adsorption to goethite at pH 4 but suppressed adsorption at pH 6 and 8. For both smectite and goethite, autunites precipitated at high phosphate and U(VI) concentrations but only after a critical supersaturation was exceeded.

Our current activities focus on U(VI)-phosphate reactions in Rifle and Hanford site sediments. Synthetic groundwaters designed to match the major element compositions at the sites were employed for both sediment types. Batch studies show little to no U(VI) sorbs to Rifle sediments except at high (1 mM) phosphate concentrations. The addition of phosphate to the influent of columns of Rifle sediments results in substantial sustained decreases in effluent U(VI) concentrations. Sequential extractions of sediments from the columns confirmed the accumulation of uranium with time and observed a gradual shift of solid-associated uranium to less mobile species. EXAFS and LIFS analysis of these sediments suggested that U(VI) was immobilized by both precipitation of an autunite mineral and adsorption. Batch studies of Hanford sediments showed distinct behavior from the Rifle sediment system. Substantial U(VI) adsorption occurred and was enhanced by phosphate addition, with an autunite-type precipitate forming at initial U(VI) and phosphate concentrations above 25 μM and 100 μM , respectively. Ongoing column experiments are investigating U(VI) retention in Hanford sediments in the presence of phosphate.

Scaling of Molecular Processes to Quantify Biogeochemical Reaction and Transport of Uranium in Subsurface Systems

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The transport of contaminants, nutrients, and dissolved constituents in water links unseen biogeochemical processes in the subsurface with natural and human-impacted surface ecosystems. Accurate prediction of the transformation, transport, and flux of dissolved contaminants such as uranium in the subsurface requires (i) identifying the kinetic or thermodynamic mechanisms that control dissolved concentrations in dynamic systems, and (ii) quantification of competing or coupled processes that may depend on aqueous speciation, solid dissolution and precipitation, surface adsorption, labile organic matter, and/or microbial catalysis. Results from batch and flow-through column experiments in sediment and model-analog systems demonstrate how laboratory investigations employing spectroscopic and genomic tools can be integrated and scaled using reactive transport modeling to quantify biotic and abiotic reaction networks.

In abiotic uranyl systems, batch and flow-through column experiments of Hanford sediment reacted with U-bearing synthetic crib waste (SCW) solutions as a function of pH, U and phosphate concentrations showed that the solubility of uranyl-phosphate phases exerts a strong thermodynamic control over U partitioning into solids. Without phosphate, U speciation was controlled by the pH-dependent rate of silicate weathering and the rate of formation of Si-bearing uranyl solids. In desorption experiments, U release in phosphate-free systems is apparently controlled by the dissolution rates of uranyl oxide hydrate phases (compreignacite, becquerelite and schoepite) and possibly U-neoformed phases. Measurement of dissolution rates of synthetic compreignacite and Na-compreignacite in flow-through columns and spectroscopic characterization of reaction products suggests that the rate-determining step is the desorption of uranyl from within an altered surface layer.

In studies of the anaerobic, oxidative dissolution of biogenically produced U(IV)-oxide, either chemical oxidants (nitrate or nitrite) or enzymatic catalysis by *Thiobacillus denitrificans*, a chemolithoautotrophic bacterium capable of nitrate-dependent U(IV) oxidation, were compared in column experiments. Uranium release was quantified using reactive transport modeling that included thermodynamic solubility, irreversible overall abiotic and biotic kinetic reactions, and uranyl sorption. Abiotic oxidation of U(IV)-oxide in the presence of nitrate under anaerobic conditions is slow but faster than control experiments of non-oxidative dissolution. Abiotic U(IV)-oxide oxidation by nitrite is significantly faster by about 1-2 orders of magnitude. In the presence of *T. denitrificans* and dissolved nitrate, higher rates of dissolved U release were observed compared with abiotic controls, suggesting that *T. denitrificans* catalyzed the oxidative dissolution of U(IV)-oxide in addition to abiotic oxidation pathways. Bacterial catalysis was supported by experiments with a mutant strain of *T. denitrificans* that was ~50% defective in enzymatic U(IV) oxidation.

Methane Oxidation in Boreal Peatlands: A Joint Field, Laboratory and Modeling Investigation

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Natural wetlands currently contribute 20-39% of global methane emissions; but their response to changing climate conditions is unknown because feedback between climate and wetland methane emissions is highly uncertain. Our objective is to improve predictions of methane emissions and constrain climate-methane feedback by focusing on the oxidation side of the methane emission equation. Specifically, we will advance understanding and modeled representations of methane oxidation within the unsaturated zone and soil zone surrounding roots of wetland plants (the rhizosphere). Rhizospheric oxidation, in particular, represents an important sink for methane, capable of oxidizing ~90% of the CH₄ produced in wetlands; however, the process is not well captured by large-scale wetland models where oxidation of CH₄ is usually simply set to a constant percentage of that transported by plants. Our approach involves fieldwork, laboratory experiments, and modeling. We are augmenting fieldwork conducted in Alaskan boreal peatlands that span hydrochemical and permafrost-thawing gradients with controlled laboratory experiments and mechanistic modeling. Results from this effort will inform the development of a dynamic representation of methane oxidation appropriate for large-scale models.

In the first year of the project, we have harnessed porewater data on concentration and isotopic composition of methane and carbon dioxide to determine rates of methane production, methane oxidation and methane loss from a subsurface profile in a boreal bog. Model fits to the data indicate that a large fraction of produced methane was not present in the porewater, suggesting it escaped to the atmosphere. However, the modeled rate at which methane was lost from the porewater far exceeded measured rates of atmospheric methane emission at the site, implying that a majority of the “lost” methane was oxidized once it left the porewater (e.g., in the unsaturated zone or in plant aerenchyma). The results indicate that methane oxidation is a key process at the site, responsible for reducing potential methane emissions by up to 98%.

Ongoing and planned field and lab work build upon these initial results by further quantifying rates of methane production, oxidation and loss within the subsurface, linking these rates to oxygen concentrations measured within the subsurface using optical oxygen sensors, and identifying factors that control subsurface oxygen concentrations. We are concurrently developing a root-scale mechanistic model that we will use to test hypotheses, aid in the quantitative assessment of field and laboratory data, and as a means for discerning the dominant controls over methane oxidation.

Microbial Dynamics in Arctic Tundra Soils: The Interplay of Plants, Soils, and Extreme Climate

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Despite the apparently harsh conditions, Arctic soils host very diverse microbial communities that are well adapted to this environment. As in other biomes, these communities are influenced by factors such as substrate chemistry, nutrient availability, and microclimate. In the rhizosphere, they are strongly influenced by plant activities, especially during the short growing season. I will review current knowledge on the factors that structure these communities and how these change across the growing season. I will also link these microbial dynamics to soil decomposition and soil formation. Finally, I will apply this framework to the role of soil microbes in ecosystem response to climate change.

Strikingly Different Form of Organic Carbon in Soils of Temperate and Permafrost Soils: Implications for Carbon and Metal Cycling

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Soils are major reservoirs of organic carbon (OC), and play a central role in the mobility of carbon between the land and the atmosphere. Among different soils, a significant fraction of global soil OC is stored in permafrost soils, and thawing and rapid losses of OC in the form of CO₂, associated with warming of polar regions, raises a serious concern for the stability of carbon in polar soils. Studies have shown that variations in soil mineralogy and biogeochemistry, and climatic conditions can modify the soil OC retention, which in turn alter the elemental cycles. The focus of our research is on how variations in vegetation and soil biogeochemical conditions control the dynamics of OC and associated major and trace elements in soils of different climatic conditions.

In this study, we examined OC forms associated with soils of temperate and polar climates using X-ray Absorption and NMR spectroscopic techniques, and high-resolution FT-ICR ESI-mass-spectrometry. In addition, to assess OC dynamics, we also evaluated the forms of S, P, and Cl bound to OC, and their time-dependent concentration variations. We compared the chemistries of these elements in Arctic soils with soils collected from temperate coniferous and deciduous forests.

Our studies indicate that the organic carbon is rich in lipids, and poor in aromatic and carboxylic carbon in the high Arctic soils when compared to soils of other climates. The O/C ratios of the extractable organic carbon also indicate that it is O-poor. This is in direct contrast to the organic matter found in soils of tropical and temperate climates, which is rich in lignins, tannins, and other condensed aromatics. The abundance of such a lipid-rich OC in high Arctic soils may be attributed to the moss, algae and fungal (or lichen) mats, whereas lignin and other aromatic-rich vascular plants are the common sources of OC in other climatic regions. Such a contrasting composition of OC in Arctic soils when compared to others suggests that these soils respond differently to temperature changes, and also interact differently with major and trace elements. We are evaluating how these different pools of OC modifies the cycling of nutrients, such as Fe, Mn, and the solubility and speciation of contaminants, such as Hg. A discussion on the contrasting forms of OC found in soils of different climates and their role in elemental cycles will be presented.

Fate of Uranium During Transport Across the Groundwater-Surface Water Interface

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Discharge of contaminated groundwater to surface waters is of concern at many DOE facilities. For example, at the Savannah River Site (SRS), uranium contaminated groundwater is discharging into natural wetlands. The numerous sharp biogeochemical transitions occurring in wetlands have profound effects on the ultimate fate of redox-sensitive trace metals and radionuclides, including uranium.

The goal of this research is to provide new insights on how plant-induced alterations to the sediment biogeochemical processes affect key uranium reducing microorganisms, uranium reduction, and uranium spatial distribution. We have formulated the following hypotheses. (1) U(VI) discharged from ground- to surface-waters can be immobilized effectively as U(IV) in the sediments at the groundwater-surface water interface. The electron donor required to stimulate the microorganisms capable of reducing U(VI) is provided by wetland plants via their root exudates and root turnover. (2) Oxygen released into the sediments by plants reoxidizes Fe(II), forming iron oxy(hydroxi)des, which provide the bioavailable Fe(III) for long-term bacterial iron-reducing activity, which is key for a sustained biological uranium reduction.

To test the above hypotheses, we operated small-scale wetland mesocosms to simulate the discharge of uranium-contaminated groundwater to surface waters. The mesocosms were operated for 80 days, followed by analysis for solid-associated chemical species, microbiological characterization, micro-X-ray florescence (μ -XRF) mapping of Fe and U on the root surface, and U speciation via X-ray Absorption Near Edge Structure (XANES).

Bacterial numbers including *Geobacter* sp., Fe(III), as well as total uranium, were highest on roots, followed by sediments near roots, and lowest in zones without much root influence. Results from the μ -XRF mapping on root surfaces indicated a strong spatial correlation between Fe and U, while the analysis via XANES showed that a significant fraction of uranium was reduced to U(IV), indicating that iron cycling in the rhizosphere also results in uranium reduction and immobilization. Under high iron loading, results indicate that co-precipitation of U(VI) with iron might have been an important U removal process.

A series of depth-discrete dialysis samplers were set up in an uranium-contaminated wetland on the SRS to monitor seasonal U dynamics. Vertical profiles of dissolved U are consistent with our laboratory findings, indicating that during the growing season when there is more active iron reduction, the dissolved U in the sediment pore water is significantly lower.

Model-Data Synthesis of Ecosystem Responses to Elevated CO₂: From Deserts to Temperate Forests of the U.S.

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There is a huge range in Earth-system model predictions of terrestrial ecosystem feedback on atmospheric CO₂ increase, and responses to elevated CO₂ (eCO₂) are a primary driver of this uncertainty [Friedlingstein et al., 2006; Arora et al., 2013]. The aims of the Free Air CO₂ Enrichment (FACE) model data synthesis (FACE-MDS) project are to evaluate terrestrial ecosystem models, focusing on the under-lying assumptions and hypotheses of the models, against data from eCO₂ experiments.

Six long-term, ecosystem-scale, eCO₂ experiments were simulated by a suite of 11 terrestrial ecosystem models. Initially the project simulated the evergreen needleleaf Duke Forest FACE experiment (NC) and the deciduous broadleaf Oak Ridge FACE experiment (TN). Recently we have included four additional sites - the evergreen broadleaf Kennedy Space Center Open Top Chamber (OTC) experiment (FL), the prairie heating and FACE experiment (WY), the Nevada desert FACE experiment and the deciduous broadleaf Rhinelander FACE experiment (MI). The presentation will focus on results from Duke and Oak Ridge.

Under ambient CO₂ conditions most models reproduced net primary productivity (NPP) with some degree of accuracy, though there were biases. Some models achieved a good fit to the observations but with compensating biases in component variables. In response to eCO₂, nitrogen (N) dynamics were the main constraint on simulated productivity. At Oak Ridge some models reproduced the declining response of C and N fluxes, while at Duke none of the models were able to maintain the observed sustained responses. C and N cycles are coupled through a number of complex interactions, which causes uncertainty in model simulations in multiple ways. Nonetheless, the major difference between models and experiments was a larger than observed increase in N-use efficiency and lower than observed response of N uptake. The results indicate that at Duke there were mechanisms by which trees accessed additional N in response to eCO₂ that were not represented in the models. Sequestration of the additional productivity under eCO₂ into forest biomass depended largely on C allocation assumptions.

In a conceptual study, using the models to simulate responses to eCO₂ over 300 years, N cycle assumptions caused the biggest variability in C sequestration across models, followed by C partitioning assumptions. A key difference between models, leading to qualitatively different responses of C sequestration, was whether N uptake was a function of N demand. By reducing N losses, demand based N uptake resulted in increased ecosystem N and sustained productivity responses to eCO₂.

Integrating Microbial Ecology with Hydro-Biogeochemistry

James Stegen (James.Stegen@pnnl.gov) - PNNL, John Zachara (PI).

As an integrated Science Focus Area (SFA) the PNNL SBR-SFA works to understand how water-cycle-driven hydrodynamics interact with fundamental biogeochemical and ecological processes across scales. Research activities focus on the zone of groundwater-surface water mixing (the subsurface interaction zone, SIZ) due strong a strong influence of this zone on contaminant release to surface waters and C/N cycling. The PNNL SFA will ultimately encode knowledge of SIZ processes in a multiscale modeling framework that forecasts system responses and feedbacks to environmental change. A challenge in the development of such a modeling framework is the need for deeper knowledge of interactions among microbial communities, major ecological factors, hydrodynamics, and biogeochemical processes. Significant advances in our understanding of these interactions have been achieved within the PNNL SFA through development of new ecological modeling frameworks and by using the Hanford 300 Area “coupled to the adjacent Columbia River” as a model system of SIZ dynamics. Relative to pre-existing approaches, our ecological modeling frameworks greatly improve understanding of factors that govern microbial communities through space and time. We find that dominant ecological factors vary across geologic formations, with selection-based processes dominating microbial communities in a fine-grained geologic formation and dispersal-effects dominating in a coarse-grained formation. We also find substantial spatial variation in the relative influences of ecological factors and reveal environmental features that may cause these variations. By further extending our modeling framework beyond community composition we show that high dispersal rates homogenize the metabolic potential of microbial communities through space, time, and across a broad range of groundwater-surface water mixing conditions. Simulation modeling predicts that this situation “where high dispersal rates govern microbial communities” causes a decline in biogeochemical rates, relative to the rates expected when selection is dominant. Integrated spatiotemporal monitoring of the SIZ nonetheless reveals that groundwater-surface water mixing causes an increase in microbial metabolism that strongly influences both carbon cycling and contaminant (nitrate) dynamics. To generate a foundation of knowledge needed to develop a predictive multiscale modeling framework, future research activities will explicitly couple spatiotemporal variation in dominant ecological factors with fundamental biogeochemical processes and will elucidate this coupling across scales.

The Challenges and Opportunities for Extending Plant Genomics to Climate Research and Modeling

David Weston (westondj@ornl.gov) - Oak Ridge National Lab (PI).

Our inability to accurately represent plant functional traits (e.g., those traits governing productivity) for a wide array of taxa and the interaction of those traits with variable environmental conditions are considered key uncertainties in land-surface models including the DOE BER funded Community Land Model (CLM). Given the importance of this issue, it is unfortunate that the scientific community is not currently leveraging advances in genomics and genetics to better predict plant traits that govern species' performance under variable climatic conditions. In this presentation, we propose an alternative strategy by incorporating high-resolution genomic-based modeling efforts for inclusion into climate models. We will illustrate this strategy with a use-case exemplifying a key plant-microbe interaction governing C and N cycling in a critical peatland ecosystem. Such a strategy has the potential to lessen the current disconnect between the genomic and climate modeling efforts, and thereby set the precedent where advances from biological system research are brought to bear in climate system research.

Hydraulic Redistribution of Water through Plant Roots and Implications for Carbon Cycling and Energy Flux at Multiple Scales

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Hydraulic redistribution (HR) of soil water by plants occurs in seasonally dry ecosystems worldwide. During drought, water flows from deep moist soil, through plant roots, into dry (often litter-rich) upper soil layers. Using measurements and modeling, we are exploring small- and large-scale effects of HR on soil water content, microbial activity, and net ecosystem carbon and energy exchange, in seasonally dry ecosystems of the Western U.S.

At the single root scale, we have modeled a 10-cm radial soil domain, with root at center, and simulated solute transport, soil cation exchange, and root exudation and nutrient uptake under two water flow patterns: daytime transpiration without nighttime HR, and daytime transpiration with nighttime HR. During HR, water efflux flushed solutes away from the root, widening depletion zones for key nutrients like nitrate. Outward transport of cations (previously accumulated near the root by transpiration) led to competitive desorption of ammonium from soil further from the root and generation of hotspots of ammonium availability at night. A microbial community and small food web will next be embedded into this dynamic resource landscape to explore how organisms responsible for nutrient and soil carbon cycling respond to these fluctuating resource regimes.

At the ecosystem scale, we have folded Ryel et al.'s (2002) HR formulation into CLM4.5 and examined how well the combined model can simultaneously simulate measured evapotranspiration, the vertical profile of soil moisture, and the amplitude of HR-associated diel changes in water content, at multiple seasonally-dry Ameriflux sites: Wind River Crane (US-Wrc), Southern California Climate Gradient (US-SCs,g,f,w,d,&c), and Santa Rita Mesquite Savanna (US-SRM). In many cases, the combined model reproduced seasonal and diel observations with reasonable accuracy. However, two shrub and one desert sites proved challenging, for as-yet unknown reasons, though at all sites, soil moisture sensors sample from a small fraction of the eddy flux tower footprint, and in at least one site, groundwater in fractured bedrock (not considered in our model) is the source of water for HR. Our next step is to explore how biogeochemistry in soil layers is affected by the inclusion of HR in CLM4.5.

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Multiscale Modeling of Ecosystem Structure and Function

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The dynamics of biological systems, from cells to communities and ecosystems, have been hypothesized to follow optimal trajectories shaped by selection pressure that force organisms to maximize their fitness and reproductive success. This concept has been particularly successful in explaining the form and function of terrestrial vegetation from eco-hydrological and carbon-economy perspectives, and across spatial and temporal scales. Any optimality model is based on three key ingredients: an objective function that describes the gain that needs to be maximized or loss to be minimized, a control variable that shifts the dynamics in the desired direction, and a set of constraints that account for environmental conditions and conservation laws bounding the system. All three ingredients are difficult to define and quantify - especially in complex biological and ecological systems. Despite these difficulties, optimality approaches may complement process-based approaches when mechanistic knowledge is scarce. At the leaf scale, it is often hypothesized that carbon gain is maximized, thus providing a quantifiable objective for a mathematical definition of optimality conditions. Eco-physiological trade-offs and fluctuating resource availability introduce natural bounds to this optimization process. In particular, carbon uptake from the atmosphere is inherently linked to root-water uptake from the soil. Hence, the multi-scaled fluctuations in soil moisture do constrain the amount of carbon assimilated into new biomass. The problem of maximizing photosynthesis at a given water availability by modifying stomatal conductance, the plant-controlled variable to be optimized, has been traditionally formulated for short time intervals over which soil moisture changes can be neglected. This simplification led to a mathematically open solution, where the undefined Lagrange multiplier of the optimization (equivalent to the marginal water use efficiency) is determined via data fitting in an ad-hoc manner. Here, a set of models based on different assumptions that account for soil moisture dynamics over an individual dry-down are proposed so as to provide closed analytical expressions for the carbon gain maximization problem for varying soil moisture resources, atmospheric CO₂ levels, and vapor pressure deficit. Bridging these theories with widely used empirical formulations of stomatal conductance in climate models are also discussed.

B4WarmED: Warming X Rainfall Manipulation Shifts Integrated Soil and Plant Community Processes in a Boreal Ecotone Experiment

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The Boreal Forest Warming at an Ecotone in Danger (B4WarmED) experiment addresses the potential for projected climate change to alter many aspects of forest function at the boreal-temperate forest ecotone. The study includes thousands of juveniles of multiple tree species growing intermixed with native vegetation on a total of 72 plots at two sites in northeastern Minnesota, with two canopy conditions (open and understory), and three levels of both aboveground and belowground warming (ambient, +1.7°C, +3.4°C) implemented for ~8 months each year since 2009. In 2012 and 2013 we began a sub-experiment whereby half of the open plots received ~45% fewer summer rain events (and rainfall) by using moveable rain curtains. In this presentation we discuss impacts of warming and rainfall manipulation on integrated soil and plant processes. The warming (infrared lamps aboveground, buried cables below) manipulation did not directly influence the amount of water vapor in the air in the plots (i.e. the vapor pressure was similar) or the relationship between air and leaf temperature, hence vapor pressure deficit (VPD) differences were solely a function of temperature differences. Therefore, at each rainfall level, the experiment is effective at testing potential impacts of warming (including indirect effects by increasing evaporative demand) in a future world where the total amount of atmospheric moisture was unchanged. Warmed plots had lower soil moisture during dry periods due to greater VPD (and secondarily due to differences in leaf area index) and as expected, such periods were heightened in the low rainfall treatment. We examined interactions of warming x rainfall on soil moisture, soil CO₂ flux, and soil microbial and animal communities, and how these collectively shape the warming treatment effects on growth and survival of the planted tree seedlings and the phenology of both those seedlings and of native herbs and low shrubs.

Carbon and Energy Balance Consequences of Widespread Mortality in Pinon-Juniper Woodlands

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The southwestern United States experienced an extended drought from 1999-2002 which led to widespread coniferous tree mortality throughout New Mexico, Arizona, Utah and Colorado. Piñon-juniper (PJ) woodlands, which occupy 24 million ha throughout the Southwest, proved to be extremely vulnerable to this drought, experiencing 40 to 95% mortality of piñon pine (*Pinus edulis*) and 2-25% mortality of juniper (*Juniperus monosperma*) in less than 3 years (Breshears et al., 2005). Understanding the response trajectories of these woodlands is crucial given that climate projections for the region suggest that episodic droughts, and associated conifer mortality, are likely to increase in frequency and severity in the coming century. We used a combination of eddy covariance, high-resolution remotely sensed datasets including full waveform lidar, soil respiration, sap flow and biomass carbon pool measurements made at an undisturbed PJ woodland (control) in central New Mexico and at a manipulation site within 2 miles of the control where all piñon trees greater than 7 cm diameter at breast height within the 4 ha flux footprint were girdled (decreasing LAI by $\sim 1/3$) to quantify the response of ecosystem carbon, water and energy fluxes in PJ woodlands to widespread piñon mortality.

As expected, piñon mortality triggered an abrupt shift in carbon stocks from productive biomass to detritus, leading to a 25% decrease in gross primary production, and >50% decrease in net ecosystem production in the two years following mortality. The girdled biome remained a carbon sink however, that was similar in strength to a nearby juniper savanna. Because piñon litter and coarse woody debris are slow to decompose in these semiarid environments, ecosystem respiration initially decreased following mortality, and only increased two years post mortality following large precipitation events. In the four years following mortality, reduced competition for water in these water limited ecosystems and increased light availability has triggered compensatory growth in understory vegetation observed in both remote sensing and ground measurements, but not in surviving coniferous trees. Changes in surface energy balance triggered by mortality are largely due to a decrease in LAI and surface roughness which decrease the redistribution of heat and energy from the surface to the atmosphere. The result is an increase in surface temperature triggered by the piñon mortality. We discuss the results in terms of feedbacks triggered by these significant mortality events on the climate system.

Resistance and Resilience of a Grassland Ecosystem to Climate Extremes

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Climate extremes, such as drought and heat waves, are forecast to be more frequent and severe with climate change. As a consequence, such events will become increasingly important drivers of future ecosystem dynamics and function. We experimentally imposed an extreme growing season drought in combination with a mid-summer heat wave over two years in a central US grassland. While the ecosystem was highly resistant to an extreme two-week heat wave, this was not the case for two years of extreme drought (with growing season precipitation totals lower than the driest two year period of the 1930s US Dust Bowl). Instead, the drought reduced aboveground net primary productivity (ANPP) below the lowest level measured in this grassland for almost thirty years, resulting in an extreme climatic event where the extreme ecological response was directly attributable to a climate extreme. The extreme reduction in ecosystem function with the two-year drought was a consequence of reduced productivity of the two dominant functional groups in this grassland - C4 grasses and C3 forbs. However, the most abundant (dominant) C3 forb was negatively impacted by the drought more than the dominant C4 grass. This differential sensitivity led to a reordering of species abundances within the plant community. Yet, despite this large shift in plant community composition, which persisted post-drought, ANPP recovered completely the year after drought. This rapid recovery in function was due to a rapid demographic response by the dominant C4 grass, which compensated for loss of the dominant C3 forb. Overall, our results suggest that low resistance of ecosystem function to an extreme climatic event does not preclude rapid ecosystem recovery. Given that dominance by a few plant species is characteristic of most terrestrial ecosystems, knowledge of the traits of these species and their responses to climate extremes will be key for predicting future ecosystem dynamics and function.

Deconvolving Local versus Regional Controls over Plant and Ecosystem Responses to Climate Change in Pacific Northwest Prairies

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Climate change is likely to shift plant range distributions and result in novel community assemblages. In turn, changes in plant community structure and ecosystem function, in particular carbon and nutrient cycling, may be closely intertwined. Furthermore, past manipulative climate change studies that have examined these issues have largely been done at a single site, and it is unclear to what extent such findings are regionally consistent.

We used a manipulative climate change experiment (increased temperature and precipitation) embedded within a 520 km natural climate gradient in the Pacific Northwest (PNW) to examine (1) the demographic responses of 12 prairie species with northern range-limits within the PNW, (2) shifts in plant community composition, and (3) carbon and nutrient cycling at three restored upland prairies for three years. For the 12 species, warming decreased the net reproductive rate, largely through a decrease in recruitment, even at the coolest edge of their current ranges, but this effect disappeared when they were moved poleward beyond their current ranges. These results are consistent with predictions that many species will need to expand their ranges poleward to successfully maintain viable populations. Warmed plots had higher abundance of annuals and introduced species, and became more similar to their southern counterparts over time, suggesting that functional group composition in PNW prairies may become similar to that currently seen in California with predicted changes in climate. Moreover, warming had a consistent positive effect on both above- and belowground NPP over the course of this study, probably due to a coincident increase in nutrient availability. Warming increased annual soil respiration by 28.6% in the northern site, 13.5% in the central site, and not at all in the southern site, reflecting the increasing degree of drought limitation from north to south in the Mediterranean climate of the PNW. Increased precipitation during the rainy season did little to alleviate drought stress and had minimal effects on range-limits, community composition, or carbon and nutrient cycling. Our results suggest that conservation planners need to (1) consider shifting species distributions and the potential need for assisted relocation with future climate change and (2) rethink the intensity of management needed to maintain native species and/or reassess feasible targets for restoration quality. The effect of warming on ecosystem processes appears to be strongly constrained by seasonal drought in these Mediterranean-climate ecosystems. Finally, our experiment demonstrates the strength of embedding manipulative climate experiments within regional climate gradients.

Geophysical Evidence for Surface-Subsurface Interactions in the Arctic Tundra

Susan Hubbard (sshubbard@lbl.gov) - Lawrence Berkeley National Laboratory, Stan Wullschleger (ORNL) (PI), Jonathan Ajo-Franklin, Baptiste Dafflon, Shan Dou, Chandana Gangodagamage, Janet Jansson, Tim Kneafsey, John Peterson, Neslihan Tas, Margaret Torn, Craig Ulrich, Marco Voltolini, Haruko Wainwright, Yuxin Wu, Stan Wullschleger (Co-Pis).

Characterized by vast amounts of carbon stored in permafrost and a rapidly evolving landscape, the Arctic has emerged as an important focal point for the study of climate change. Although recognized as an ecosystem highly vulnerable to climate change, mechanisms that govern feedbacks between the terrestrial and climate system are not well understood. As part of the NGEE-Arctic study, investigations are underway at the Barrow, AK Environmental Observatory to identify interactions that drive feedbacks to the climate system. Characterization of controlling biological, geochemical and physical processes that govern the ecosystem functioning is challenging due to the scale range over which these processes occur and interact. This presentation will discuss illustrate the use of new conceptualizations, geophysical datasets, and integration methodologies to characterize the Barrow Study Site from centimeter to kilometer length scales. The geomorphology of this tundra region is characterized by ice wedge polygons and drained thaw lake basins. We are exploring relationships between land surface, active layer, and permafrost properties using a variety of remote sensing, surface-based geophysical datasets (electromagnetic, seismic, electrical and radar), and point measurements (hydrological-geochemical-microbiological). Our results demonstrate the strong correspondence between the variability of land-surface and subsurface properties relevant to carbon cycling, which suggests that geophysically-identified co-variability can be exploited to characterize complex terrestrial environments across scales. The geophysically-identified landscape zones are providing a framework for the interpretation of carbon flux and metagenomic datasets, and are also expected to be useful for model parameterization. The rich datasets have also allowed us to document other aspects of the system that are expected to be useful for predicting the system evolution, including the influence of polygon type (high centered versus low centered) versus polygon feature (trough, rim, center) on properties that influence the microbial degradation of organic carbon (soil moisture, active layer thickness, temperature) and the presence of a deep unfrozen zone in what was originally interpreted to be the permafrost.

Geomorphological Controls on Water and Terrestrial Ecosystem Processes within Ice-Rich Polygonal Landscapes

Cathy Wilson - Los Alamos National Laboratory (PI).

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.

Multi-Disciplinary Research Targets Improved Representation of Arctic Ecosystems in Earth System Models

David Graham (grahamde@ornl.gov) - Oak Ridge National Laboratory(PI); Susan S. Hubbard, Lawrence Berkeley National Laboratory; E.A.G. (Ted) Schuur, University of Florida; Peter E. Thornton, Oak Ridge National Laboratory; Cathy J. Wilson, Los Alamos National Laboratory; Stan D. Wullschleger, Oak Ridge National Laboratory (Co-PIs).

DOE Office of Science, Climate and Environmental Sciences Division has a current goal to “Develop, test, and simulate process-level understanding of terrestrial ecosystems, extending from bedrock to the top of the vegetative canopy.”¹² Beginning several years ago, Arctic ecosystems were identified by DOE as a target for research investments due to their global importance, climatic sensitivity, and significant knowledge gaps. DOE now has major research investments in Arctic ecology. This session will highlight examples of those investments including the National Laboratory-led Next-Generation Ecosystem Experiments (NGEE) Arctic project and the university-led Carbon in Permafrost Experimental Heating Research (CiPEHR) project.

NGEE Arctic, which is now beginning its third year of research in Barrow, Alaska, is planned as a 10-year effort to deliver a process-rich ecosystem model in which the evolution of Arctic ecosystems in a changing climate can be modeled at the scale of a high resolution Earth System Model grid cell. A multi-disciplinary team is conducting research on carbon and water cycle processes associated with changing landscapes on the Arctic Coastal Plain. These complex and heterogeneous ecosystems are influenced by strong surface-subsurface interactions, topography and water distribution, and resulting effects on vegetation dynamics and biogeochemistry. The challenge here is ultimately one of process integration and scaling - how to extend understanding at core, plot, and landscape scales to the needs of models working at the kilometer scale. This requires the close collaboration of field, laboratory, and modeling research so that the knowledge gaps and structure of current models informs process research and vice versa. NGEE Arctic scientists will present a series of presentations illustrating important aspects of the project and demonstrating how this tight model-process coupling can inform and advance research in this area.

In addition, Ted Schuur will report results from five years of an ecosystem warming manipulation near Eight Mile Lake, Alaska, the CiPEHR project, which was established in 2008 to test hypotheses about expected changes in the carbon cycle as a result of warming temperatures and permafrost thaw. The CiPEHR project uses snow fences coupled with spring snow removal to increase soil and permafrost temperatures and open-top chambers to increase growing season air temperatures. Core measurements include monitoring of soil temperature and moisture, thaw depth, water table depth, and carbon dioxide fluxes, and measurements of plant productivity and phenology, soil and plant nutrient status, methane fluxes, and stable and radioactive carbon isotopes in plants and soils.

The Impact of Permafrost Carbon Loss on the Carbon Balance of an Experimentally Warmed Tundra Ecosystem

Ted Schuur (tschuur@ufl.edu) - University of Florida (PI), Sue Natali, Woods Hole Research Center; Elizabeth Webb 1; Verity Salmon 1; Marguerite Mauritz 1; Rosvel Bracho 1; Christina Schaedel 1; Jack Hutchings 1; Grace Crummer 1; Caitlin Pries, Lawrence Berkeley Lab; Elaine Pegoraro 1 (Co-PIs). 1: University of Florida

Approximately 1700 billion tons of soil carbon are stored in the northern circumpolar permafrost zone, more than twice as much carbon than currently contained 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. Yet, the rate and form of release is highly uncertain but crucial for predicting the strength and timing of this carbon cycle feedback this century and beyond. Here we report results from five 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). 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, in line with decadal trends of 'greening' tundra across the region. This response increased through the first four years of the experiment and then maintained this elevated level in year five, even though thaw depth continued to increase. 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 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. These results highlight the importance of winter processes in determining whether tundra acts as a C source or sink, and demonstrate the potential magnitude of C release from the permafrost zone that might be expected in a warmer climate. Furthermore, this initial response to warming quantifies the vulnerability of organic C stored in near surface permafrost to temperature change, and corresponds to the initial stages of permafrost degradation observed from a thaw gradient at a nearby location.

Diversity and Metabolic Potential of the Terrestrial Subsurface Microbiome and its Influence on Biogeochemical Cycling

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We are developing approaches for quantifying and simulating the interactions that govern biogeochemical cycling in terrestrial subsurface environments at genome-through-watershed scales (LBNL Sustainable Systems SFA 2.0). The terrestrial subsurface is a highly complex component of the Earth System and its biology is largely unknown. In fact, microbially mediated subsurface processes may be the least understood aspect of terrestrial biogeochemical cycling. Our approach to analysis of the microbial composition and metabolic potential of the subsurface leverages cultivation-independent DNA sequencing methods that are being applied to samples of sediment, groundwater, and field manipulation experiments from a floodplain site adjacent to the Colorado River, USA. Samples are collected from a range of depths, aquifer locations, and time periods. Our objective is to reconstruct draft and curated genomes from very large sequence datasets in order to predict the metabolic potential of each organism, in some cases coupled with proteomic and transcriptomic analyses and isolate-based experiments. Our studies have uncovered a remarkably high degree of taxonomic novelty within both the bacterial and archaeal domains and shown relatively little overlap in community composition across sampling sites. Notable is the finding of relatively unvarying metabolic potential within a radiation of many candidate phyla (CP; phyla for which no single member has been isolated). Based on more than 700 genomes from 11 of these lineages (including 12 complete, finished genomes) we predict small genome size, small cell size, low metabolic rates, limited metabolic potential, and a fermentation-based lifestyle. Based on many draft and two complete archaeal genomes, we have also defined a major subdivision within the archaeal domain; this sub-domain includes all known nanoarchaea. Genomes from the CP bacteria and archaea and for hundreds of organisms from many other lineages, encode a wide variety of metabolic traits, including the ability to fix carbon (in some cases, via novel RuBisCO-mediated pathways) and nitrogen, to reduce nitrate and/or nitrite, to oxidize sulfur, reduce sulfate, produce short-chain fatty acids, and to produce and/or use hydrogen. This information is being used, in the context of experiments and geochemical information, as inputs for the development of metabolic models to describe interactions and elemental cycling and its relation to hydrologic and geochemical fluctuations.

Omics and Geochemistry: the ENIGMA 100-Well Survey

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At the Department of Energy's Oak Ridge field site, over 20 years of historical and published data for more than 800 groundwater wells is available in a computer queryable database. In this study, we conducted a survey of 99 groundwater well clusters in order to (1) characterize key microbial populations at geochemically distinct locations, and (2) identify associations between environmental gradients and microbial communities. To optimize geochemical diversity, wells were selected using k-medians clustering to group 818 wells into 100 clusters by 14 geochemically similar measurements. At each well, in situ groundwater measurements were recorded and unfiltered and filtered groundwater samples were collected for both geochemical measurements and analysis of microbial communities. Nucleic acids were collected by filtering water through a 10.0µm pre-filter and 0.2µm-membrane filter and then extracted using a Modified Miller method. Evaluation of divergence of microbial communities across all the wells indicates the microbial communities are fairly distinct. Comparison of microbial communities within each well shows taxa are not as divergent compared to across all wells. Metadata correlations of all the wells show many of the geochemical parameters are independent of each other. To evaluate potential microbial-geochemical associations, a random forest classification system was used and trained on the OTU abundances to predict continuous values for each geochemical parameter. Results indicate that with careful design and a large dataset, the groundwater microbial community structure can be used to accurately predict the water geochemistry. This project is part of the ENIGMA (Ecosystems and Networks Integrated with Genes and Molecular Assemblies) Scientific Focus Area at LBNL (<http://enigma.lbl.gov>).

Hg(0) oxidation by Anaerobic Bacteria

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Background and Objectives: Redox cycling between elemental [Hg(0)] and divalent [Hg(II)] mercury is a key control on the fate and transport of Hg in groundwater systems. Whereas dissolved gaseous elemental mercury [Hg(0)] is mobile in groundwater, while oxidized mercuric mercury [Hg(II)] readily sorbs onto mineral surfaces and organic matter. The objectives of this study were: 1) to determine if anaerobic bacteria catalyzes the oxidation of Hg(0) to Hg(II); and 2) to determine anaerobic Hg-methylating bacteria produce MeHg when provided with Hg(0) as the sole Hg source.

Research Methods: Hg(0) oxidation experiments were carried out with the obligate anaerobic bacteria *Geothrix fermentans* H5 and *Desulfovibrio desulfuricans* ND132 and the facultative anaerobic bacteria *Shewanella oneidensis* MR-1 and *Cupriavidus metallidurans* AE104. To demonstrate the formation of Hg(II), we performed ethylation experiments and X-ray absorption near edge structure (XANES) spectroscopy on Hg(0)-reacted cell. Finally, samples from experiments conducted with the methylating bacterium strain ND132 were analyzed for the production of MeHg.

Results: All four bacterial strains reacted with dissolved gaseous Hg(0) to form non-purgeable Hg. Derivatization of non-purgeable Hg to diethylmercury and the Hg LIII-edge position of the XANES spectra demonstrated that the Hg(0)-reacted bacterial samples had formed oxidized Hg(II). XANES analysis also revealed that cell-associated Hg(II) was covalently bound to bacterial functional groups, most likely to thiol moieties. Experiments with metabolically active and heat-inactivated cells indicated that both live and dead cells oxidized Hg(0) to Hg(II). MeHg analyses showed that live cells of *D. desulfuricans* ND132 produced large quantities of methylmercury. The results of this work demonstrate a potentially important pathway in the mercury cycle, whereby anaerobic bacteria produce MeHg when provided with dissolved Hg(0) as their sole Hg source.

Sulfur-Mediated Electron Shuttling during Bacterial Iron Reduction

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Understanding the flow of electrons through various types of microbial metabolisms is essential to predicting the fate and transport of contaminants as well as the speciation and distribution of carbon in the subsurface, rhizosphere, and its release into the atmosphere. Fe(III) minerals are critical electron acceptors in many aquifers, but the extent to which they provide energy for the growth of microorganisms depends greatly on the thermodynamic energy that is available to them from their environment. In alkaline, oligotrophic aquifers, for example, the amount of energy available to dissimilatory metal-reducing bacteria (DMRB) via the reduction of Fe(III) minerals decreases dramatically with increasing pH. Many DMRB, however, can also respire by reducing elemental sulfur [S(0)] to sulfide, a process which provides more energy under alkaline conditions than acidic ones. In a series of bioreactor experiments, we have shown that at pH 9, the DMRB *Shewanella oneidensis* MR-1 can respire S(0) but not goethite. The sulfide produced subsequently reduced goethite abiotically. In experiments conducted with a mutant strain of *S. oneidensis* (PSRA1), which is able to reduce Fe(III) but not S(0), no ferrous iron was produced. The reduction of S(0) to sulfide and the formation of mackinawite (FeS) was confirmed by sulfur K-edge x-ray absorption near-edge spectroscopy (XANES). Because the abiotic reaction of sulfide with Fe(III) produces S(0), in the absence of geologic deposits of S(0), DMRB in alkaline aquifers may require active respiration by sulfate-reducing bacteria (SRB) in order to respire. Under these conditions, Fe(III) reduction will proceed via S(0)-mediated electron shuttling pathways that requires a mutualistic partnership between DMRB and SRB rather than direct enzymatic reduction of Fe(III) minerals by DMRB alone.

Experiment-inspired Software Design and Ecosystem Modular Testing for CLM Development

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One key factor in the improved understanding of earth system science is the development and improvement of high fidelity earth system models. Along with the deeper understanding of system processes, the complexity of software systems of those modelling systems becomes a barrier for further rapid model improvements and validation. In this paper, we present our software engineering practices for better understanding the Community Land Model (CLM) within an earth system modeling framework. First, we give an overview of the software system of the global offline CLM system. Second, we present our approach to better understand current CLM software structure, data structure computational characteristics using advanced software tools. After that, we focus on experiment-inspired CLM individual ecosystem function testing and new module development, such as preparations for standalone root module development. At last, we layout our plan to further engage broad user communities (modelers, field experimentalists, observation dataset providers, computer scientists, etc.) via web-services and cloud computing. Since better software engineering practices are much needed for general scientific software systems, we hope those considerations can be beneficial to many other modeling research programs involving multiscale system dynamics and legacy scientific software packages.

Expanding the Role of Reactive Transport Modeling (RTM) within the Biogeochemical Sciences

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The formation, operation, and evolution of Earth systems are complex due to the coupling of physical, chemical, and biological processes in the subsurface. Data collection and analysis coupled with field observation have provided significant insights into the factors that determine the evolution of the critical zone. Mechanistic understanding and prediction of the intimately coupled processes, however, often requires advanced modeling tools that can integrate large and diverse data sets to quantify the effects of individual processes, while at the same time provide a window into the coupled processes that may control the overall system behavior. Reactive Transport Modeling (RTM) has been used for approximately three decades to understand complex subsurface processes in many applications, including weathering and soil formation, remediation, natural attenuation, and geological carbon sequestration. RTM is now also becoming essential for the understanding of key societal issues such as “fracking”.

We organized an NSF workshop on April 13-15 in Embassy Suites Hilton in Alexandria. The goals were to (1) identify the frontiers of reactive transport in the biogeochemical sciences, and (2) determine what educational and infrastructure development is required to achieve these goals. We aimed to identify key interfaces between reactive transport modeling approaches and biogeochemical data collection and analysis. Some of the key questions included 1) What are key outstanding hypotheses that could be addressed with current capabilities? 2) What are additional modeling capabilities that would expand the scope of scientific hypotheses that can be addressed? 3) What educational tools are critically needed but are not available, and how should these be developed?

There have been a lot of interesting discussions during the RTM workshop along these lines. Currently RTM has typically been used in subsurface systems within a range of scales typically from the pore scale (10⁻⁵ meters) to field scales (10s of meters). However, the community is really pushing forward to see the coupling between subsurface RT processes to various other processes, including surface hydrology, plants, land-surface interactions, ecosystems, carbon cycling at a wider range of scales from as small as a cell to as large as the global scale. The discussions on education focused on what can be done to teach more RTM courses and help maintain the momentum for biogeochemists to include RTM in their research toolboxes.

Poster Abstract List

SBR Poster Abstracts	19
Early Career Awards	19
Multi-system Analysis of Microbial Biofilms	19
Matthew Marshall (matthew.marshall@pnnl.gov) - Pacific Northwest National Laboratory (PI), S.M. Belchik, A. E. Tucker, E.A. Hill, X. Hua, X-Y. Yu, B. Liu, Z. Wang, Z. Zhou, W.B. Chrisler, A.C. Dohnalkova; PNNL(Co-PIs).	
Computational Bayesian Framework for Quantification and Reduction of Predictive Uncertainty in Groundwater Reactive Transport Modeling	20
Ming Ye (mye@fsu.edu) - Florida State University (PI).	
Institute	21
¹⁵N and ¹⁸O Isotope Systematics of Anaerobic Abiotic Reduction of Nitrite by Iron (II)	21
Scott Wankel (sdwankel@whoi.edu) - Woods Hole Oceanographic Institution - project leader, David Johnston - Harvard University (PI); Carolyn Buchwald - Woods Hole Oceanographic Institution; Colleen Hansel - Woods Hole Oceanographic Institution; David Johnston - Harvard University (Co-PIs).	
Scientific Focus Areas (SFA).....	22
Interconnected Cycling of Fe, S, and C in the Terrestrial Subsurface: New Paths and Opportunities for Coupling Biotic and Abiotic Processes	22
Dionysios Antonopoulos (dantonopoulos@anl.gov) - Argonne National Laboratory, Edward J. O'Loughlin (PI), Theodore M. Flynn (ANL); Kim M. Handley (ANL); Man Jae Kwon (ANL); Daniela Bartels (ANL); Maxim I. Boyanov (ANL); Folker Meyer (ANL); Bhoopesh Mishra (ANL); William L. Trimble (ANL); Philip E. Long (LBNL); Kenneth H. Williams (LBNL); Thomas J. DiChristina (Georgia Institute of Technology); Kenneth M. Kemner (ANL) (Co-PIs).	
Characterizing Biogeochemical Hot Spots and Hot Moments in a Floodplain System	23
Bhavna Arora (barora@lbl.gov) - Lawrence Berkeley Laboratory (PI), Haruko M. Wainwright, LBL; Dipankar Dwivedi, LBL; Carl I. Steefel, LBL; Eoin Brodie, LBL; Alexis Navarre-Sitchler, CSM; Rodrigo Prugue, CSM; Amy Kenwell, CSM; Kenneth H. Williams, LBL; Susan Hubbard, LBL (Co-PIs).	
Sustainable Systems SFA 2.0: Extensive Genome-Resolved Analyses Reveal Roles for Uncultivated Archaea and Bacteria in Subsurface Biogeochemical Cycling.....	24
Jillian Banfield (jbanfield@berkeley.edu) - UC Berkeley (PI), Harry R. Beller (LBNL); Eoin L. Brodie (LBNL); Mike J. Wilkins (PNNL); Kenneth H. Williams (LBNL) (Co-PIs).	
SLAC SFA: Coupled Cycling of Organic Matter, Uranium, and Biogeochemical Critical Elements in Subsurface Systems.....	25
John Bargar (bargar@slac.stanford.edu) - SLAC National Accelerator Laboratory -Project Leader (PI), Scott Fendorf ² , Chris A. Francis ² , Alfred M. Spormann ² , Sharon E. Bone ¹ , Noemie Janot ¹ , and Morris E. Jones ² ; (Co-PIs). Affiliations: ¹ SLAC National Accelerator Laboratory, ² Stanford University.	
SLAC SFA: Characterization of Uranium and Biogeochemical Critical Elements in Organic-Rich Sediments.....	26
John Bargar (bargar@slac.stanford.edu) - SLAC National Accelerator Laboratory- Project Leader (PI), Sharon E. Bone ¹ , Noemie Janot ¹ , Scott Fendorf ² , Morris E. Jones ² , Kenneth H. Williams ³ , Philip E. Long ³ , Stan D. Wulfschleger ⁴ , Elizabeth Herndon ⁴ , and Baohua Gu; (Co-PIs). Affiliations: ¹ SLAC National Accelerator Laboratory, ² Stanford University, ³ Lawrence Berkeley National Laboratory, ⁴ Oak Ridge National Laboratory.	

Uranium Biogeochemistry in Organic-Rich Sediments: Laboratory Analog Studies.....	27
John Bargar (bargar@slac.stanford.edu) - SLAC National Accelerator Laboratory (PI), Scott Fendorf, Stanford University; Morris E. Jones, Stanford University; Sharon Bone, SLAC National Accelerator Laboratory (Co-PIs).	
Chemolithoautotrophy in the Rifle subsurface relevant to C, S, and Fe cycling	28
Harry Beller (HRBeller@lbl.gov) - LBNL (PI), Jillian Banfield (UC Berkeley); Eoin Brodie (LBNL); Kenneth Williams (LBNL); Michael Wilkins (Ohio State University); Robert Hettich (ORNL) (Co-PIs).	
Microbial Sorption of Plutonium and the Role of Extracellular Polymeric Substances	29
Mark Boggs (boggs6@llnl.gov) - Lawrence Livermore National Laboratory, Mark Antony Boggs (PI), Annie Kersting; Mavrik Zavarin (Co-PIs).	
Redox Dynamics of Hg and U: Mn(II) as a Reductant of Hg(II) and the Influence of Mineral Surface Sites on the Speciation of U(IV).....	30
Maxim Boyanov (mboyanov@anl.gov) - Argonne National Laboratory 2- Project component leader (PI); Co-PIs: Bhoopesh Mishra ^{1,3} ; Drew Latta ^{1,4} ; Ed O'Loughlin ¹ ; Ken Kemner ¹ ; 1. Biosciences Division, Argonne National Laboratory; 2. Institute of Chemical Engineering, Bulgarian Academy of Sciences; 3. Department of Physics, Illinois Institute of Technology; 4. Department of Civil and Environmental Engineering, University of Iowa.	
Diel mercury-concentration variations in a mercury impacted stream.....	31
Scott Brooks (brookssc@ornl.gov) - Oak Ridge National Laboratory (PI), Ami L. Riscassi (ORNL- University of Virginia); Carrie L. Miller (ORNL) (Co-PIs).	
PNNL SBR SFA: Data Management and Assimilation	32
Xingyuan Chen (xingyuan.chen@pnnl.gov) - Pacific Northwest National Laboratory (PI), Glenn E. Hammond, SNL; Tim Johnson, PNNL (Co-PIs).	
Iron and organic matter dynamics under fluctuating redox conditions	33
Cristina Cismasu (accismasu@lbl.gov) - Lawrence Berkeley National Laboratory, P.S. Nico (PI), P.S. Nico, LBNL, project leader; K.H. Williams, LBNL (Co-PIs).	
Isotopic Evidence for Biogeochemical Interactions Between the Unsaturated Zone and Groundwater in the Rifle Floodplain	34
Mark E. Conrad (msconrad@lbl.gov) - Lawrence Berkeley National Laboratory, Susan Hubbard (PI), John N. Christensen (LBNL); Markus Bill (LBNL); Jiamin Wan (LBNL); Kenneth H. Williams (LBNL); Tetsu K. Tokunaga (LBNL) (Co-PIs).	
Organismal and Environmental Level Investigations of the Mercury Methylating Genes hgcAB	35
Dwayne Elias (eliasda@ornl.gov) - Oak Ridge National Laboratory, Scott Brooks (PI), Richard A. Hurt Jr. ¹ , Anil C. Somenahally ¹ , Romain Bridou ³ , Steven D. Smith ³ , Mircea Podar ¹ , Steven D. Brown ¹ , Craig C. Brandt ¹ , Anthony V. Palumbo ¹ , Judy D. Wall ³ , Cynthia C. Gilmour ² ; (Co-PIs). 1 Oak Ridge National Laboratory.; 2 Smithsonian Environmental Research Center; 3 University of Missouri, Department of Biochemistry.	
Molecular Biology Level Investigations of the Mercury Methylating Genes hgcAB.....	36
Dwayne Elias (eliasda@ornl.gov) - Oak Ridge National Laboratory, Scott Brooks (PI), Richard A. Hurt Jr. ¹ , Anil C. Somenahally ¹ , Romain Bridou ³ , Steven D. Smith ³ , Mircea Podar ¹ , Steven D. Brown ¹ , Jerry M. Parks ¹ , Alexander Johs ¹ , Craig C. Brandt ¹ , Anthony V. Palumbo ¹ , Judy D. Wall ³ , Cynthia C. Gilmour ² ; (Co-PIs). 1 Oak Ridge National Laboratory.; 2 Smithsonian Environmental Research Center; 3 University of Missouri, Department of Biochemistry.	
Identification and quantification of mercury binding functional groups in natural organic matter and methylating bacteria	37
Baohua Gu (gub1@ornl.gov) - Oak Ridge National Laboratory (PI), Benjamin Mann; Hui Lin; Balaji Rao; Liyuan Liang (Co-PIs).	
System Fluxes: Task 1	38
Maoyi Huang (maoyi.huang@pnnl.gov) - PNNL, (PI).	

The LBNL Sustainable Systems Subsurface Biogeochemistry SFA 2.0: Overview.....39

Susan Hubbard (sshubbard@lbl.gov) - Lawrence Berkeley National Laboratory (PI), Jillian F. Banfield (UCB/LBNL), Harry R. Beller (LBNL), Eoin Brodie (LBNL), Phillip E. Long (LBNL), Peter Nico (LBNL), Carl Steefel (LBNL), Tetsu Tokunaga (LBNL), Kenneth H. Williams (LBNL), Deb Agarwal (LBNL); and the SFA 2.0 Team; (Co-PIs).

The Molecular Basis of Mercury Methylation: Expression, Purification and Characterization of HgcA40

Alexander Johs (johsa@ornl.gov) - Oak Ridge National Laboratory, Scott Brooks (PI), D. Riccardi, A. Belic, - ORNL;; S. J. Tomanicek - UTK;; R. Bridou, S. D. Smith, J. D. Wall - U. Missouri; J. M. Parks, D. A. Elias, Jeremy C. Smith (project lead) - ORNL/UTK (Co-PIs).

Synchrotron-based characterization of the physical and chemical characteristics of carbon in the subsurface and root zones to improve Earth system modeling of biogeochemical cycling of carbon41

Ken Kemner (kemner@anl.gov) - Argonne National Laboratory (PI), B. Mishra (Illinois Institute of Technology & ANL); E. J. O'Loughlin (ANL); M. I. Boyanov- (Bulgarian Academy of Sciences & ANL); S. O'Brien (ANL); V. Bailey (PNNL); A. Konopka (PNNL); J. Jastrow (ANL); C. Liang (ANL); M. Balasubramaniam (ANL); R. Gordon (ANL); B. Cooper (Florida State University); J. Chanton (Florida State University); M. Tffaly (PNNL and Florida State University) (Co-PIs).

Identifying Molecular Scale Mechanisms Controlling Actinide Transport.....42

Annie Kersting (kersting1@llnl.gov) - Lawrence Livermore National Laboratory (PI), Mavrik Zavarin (lead scientist); Brian Powell (Clemson Univ.); (Co-PIs).

LBNL Sustainable Systems SFA 2.0: Genome-enabled watershed simulation capability (GEWaSC).....43

Eric King (eking@lbl.gov) - Lawrence Berkeley National Laboratory, Susan Hubbard (PI), S. Molins1, U. Karaoz1, N.J. Bouskill1, L.A. Hug2, B.C. Thomas2, C.J. Castelle2, H.R. Beller1, J.F. Banfield2, C.I. Steefel1, E.L. Brodie1 (Co-PIs). 1 LBNL, 2 ORNL, 3University of California, Berkeley.

Microbial cell surface interactions and biogeochemical controls on mercury (Hg) redox transformation and methylation.....44

Hui Lin (linh1@ornl.gov) - Oak Ridge National Lab (PI), Balaji Rao; Benjamin Mann; Dwayne Elias; Liyuan Liang; Baohua Gu (project leader) (Co-PIs).

Hydro-Biogeochemical Process Dynamics in the Groundwater-Surface Water Interaction Zone: Fundamental Mechanisms and Mechanism-based Models45

Chongxuan Liu (Chongxuan.liu@pnnl.gov) - Pacific Northwest National Laboratory (PI), Hyun-Seon Song; Liang Shi; William Nelson; Kevin Rosso; Jim Fredrickson; John Zachara (Co-PIs).

Characteristics of the Hanford Reach of the Columbia River Groundwater-Surface Water Interaction Zone for Investigating Hydro-Biogeochemical Process Dynamics.....46

Chris Murray (chris.murray@pnnl.gov) - Pacific Northwest National Laboratory, John Zachara (PI), Jim Fredrickson (PNNL); Tim Scheibe (PNNL) (Co-PIs).

Hydro-Biogeochemical Process Dynamics in the Groundwater-Surface Water Interaction Zone: Macroscopic Processes47

William Nelson (william.nelson@pnnl.gov) - PNNL, John Zachara (PI), James Stegen (Project Leader); Glenn Hammond; Eric Roden; Tim Johnson; Evan Arntzen; Xingyuan Chen; Chris Murray; Tim Scheibe; James Fredrickson; John Zachara (Co-PIs).

Organic-Mineral Dynamics Component of LBNL SFA2.048

Peter Nico (psnico@lbl.gov) - LBNL, Susan Hubbard (LBNL) (PI), Cristina Cismasu (LBNL); Patricia Fox (LBNL); Ben Gilbert (LBNL); Jim Davis (LBNL) (Co-PIs).

Geochemical and microbiological response to oxidant introduction into reduced Hanford 300 Area sediments49

Eric Roden (eroden@geology.wisc.edu) - University of Wisconsin-Madison (PI), Elizabeth M. Percak-Dennett, University of Wisconsin-Madison; Allan E. Konopka, and James P. MicKinley, Pacific Northwest National Laboratory (Co-PIs).

Redox Transition Zone Phyllosilicate Reactivity: Thermodynamics and Microscopic Processes50

Kevin Rosso (kevin.rosso@pnnl.gov) - Pacific Northwest National Laboratory, Andrew Felmy (PI); Kevin Rosso (PI) (PI), Odeta Qafoku, PNNL; Mark Bowden, PNNL; Vitali Alexandrov, PNNL; Carolyn Pearce, U. of Manchester; Eugene Ilton, PNNL; Chongxuan Liu, PNNL (Co-PIs).

Multiscale Science and Modeling: Task 4.....51

Timothy Scheibe (tim.scheibe@pnnl.gov) - Pacific Northwest National Laboratory, John Zachara (PI), Ilenia Battiato (Clemson University); Alexander Tartakovsky (PNNL); Chongxuan Liu (PNNL); Xingyuan Chen (PNNL); Maoyi Huang (PNNL) (Co-PIs).

Microbial Extracellular Electron Transfer Mechanism in Hanford Subsurface Geobacter spp.....52

Liang Shi (liang.shi@pnnl.gov) - Pacific Northwest National Laboratory (PI), Yimo Liu¹, Zheming Wang¹, Juan Liu¹, Caleb Levar², Marcus J. Edwards³, Jerome T. Babauta⁴, David W. Kennedy¹, Zhi Shi¹, Eric E. Roden⁵, Haluk Beyenal⁴, Daniel R. Bond², Thomas A. Clarke³, Julea N. Butt³, David J. Richardson³, Kevin M. Rosso¹, John M. Zachara¹ and James K. Fredrickson¹; (Co-PIs). ¹ PNNL, ² University of Minnesota, ³ University of East Anglia, ⁴ Washington State University, ⁵ University of Wisconsin-Madison.

Determining Mechanisms of Hg Methylation by HgcA and intramolecular Hg transfer by MerA at the Atomic Scale53

Jeremy Smith (smithjc@ornl.gov) - Oak Ridge National Laboratory (PI), Project Leader: Scott C. Brooks, ORNL; Ariana Beste, UTK; Hao-Bo Guo, ORNL; Hong Guo, UTK; Alexander Johs, ORNL; Susan M. Miller, UCSF; Jerry M. Parks, ORNL, UTK; Demian Riccardi, ORNL; Anne O. Summers, UGA; Stephen J. Tomanicek, UTK; Jing Zhou, UTK (Co-PIs).

Water and carbon fluxes into groundwater from a semi-arid floodplain vadose zone.....54

Tetsu Tokunaga (tktokunaga@lbl.gov) - Lawrence Berkeley National Laboratory (PI), Jiamin Wan*, Wenming Dong*, Kenneth H. Williams*, Mark J. Robbins*, Yongman Kim*, Boris Faybishenko*, Mark E. Conrad*, John N. Christensen*, Chad Hobson*, Benjamin Gilbert*, Richard Dayvault (Stoller Corp.); Philip E. Long*, Susan S. Hubbard* (Project Lead); (*LBNL) (Co-PIs).

Sustainable Systems SFA Data Management and Assimilation55

Charuleka Varadharajan (cvaradharajan@lbl.gov) - Lawrence Berkeley National Laboratory, Deborah Agarwal, Lawrence Berkeley National Laboratory (PI), Roelof Versteeg, Subsurface Insights; Boris Faybishenko, Lawrence Berkeley National Laboratory (Co-PIs).

Capturing Transient Climate-Driven Contributions of Surface to Subsurface Processes at Watershed Scales.....56

David Watson (watsondb@ornl.gov) - Oak Ridge National Laboratory, Scott Brooks (PI), Scott Brooks - ORNL Project Lead, Guoping Tang - ORNL, Chris Schadt - ORNL, Nathan Collier - ORNL, Pengsong Li - Peking University, and Fengming Yuan - ORNL (Co-PIs).

Floodplains as biogeochemical reactors: Using multi-scale approaches to quantify hot spots and hot moments at DOE's Rifle, Colorado field site.....57

Kenneth Williams (khwilliams@lbl.gov) project leader - LBNL, Susan S. Hubbard (LBNL)(PI), Adrian Flores Orozco (Technical University of Vienna), Matthias Bucker (Univ. of Bonn), Chad Hobson (LBNL), Haruko Wainwright (LBNL), Baptiste Dafflon (LBNL), Mark Conrad (LBNL), Tetsu Tokunaga (LBNL), John Bargar (SSRL), (Co-PIs).

Seasonal Hydrology and Biogeochemical Hot Spots: Carbon, Nitrogen and Mineralogic Controls on Suboxic Conditions in the Rifle Floodplain Aquifer.....58

Steve Yabusaki (yabusaki@pnnl.gov) – PNNL (PI), B. Arora, LBNL; N.F. Spycher, LBNL; S. Molins, LBNL; R.M. Maxwell, Colorado School of Mines; J. Beisman, Colorado School of Mines; A. Navarre-Sitchler, Colorado School of Mines; Y. Fang, PNNL; E.L. Brodie, LBNL; C.I. Steefel, LBNL; S.S. Hubbard, LBNL Project Leader; Sustainable Systems SFA 2.0 Science Team (Co-PIs).

Pacific Northwest National Laboratory SFA: Hydro-Biogeochemical Process Dynamics in the Groundwater-Surface Water Interaction Zone	59
John Zachara (john.zachara@pnnl.gov) - PNNL (PI); Jim Fredrickson, PNNL; Tim Scheibe, PNNL; Xingyuan Chen, PNNL; Glenn Hammond, SNL; Maoyi Huang, PNNL; Chongxuan Liu, PNNL; Chris Murray, PNNL; James Stegen, PNNL; Charlette Geffen, PNNL (Co-PIs).	
<i>Student Abstracts</i>	60
Speciation of uranium controls its kinetics of reduction by metal-reducing bacteria.....	60
Keaton Belli (keaton.belli@gatech.edu) - Georgia Institute of Technology, Martial Taillefert (PI), Georgia Tech School of Earth and Atmospheric Sciences; Philippe Van Cappellen, University of Waterloo Department of Earth and Environmental Sciences; Carl Steefel, Lawrence Berkeley National Laboratory (Co-PIs).	
Extensive genomic sampling of subsurface microbes provides a new view of the phylogeny and metabolic potential of the bacterial Candidate Phyla OD1 and OP11	61
Christopher Brown (ctb@berkeley.edu) - UC Berkeley, Jillian F. Banfield (PI).	
Organic Matter Sources in the Speciation and Mobilization of Pu in the Subsurface Environment of the Rocky Flats Site	62
Nicole DiDonato (ndidonat@odu.edu) - Old Dominion University, Dr. Peter Santschi (PI), Dr. Patrick Hatcher, ODU; Dr. Chen Xu, TAMUG; Dr. Kathleen A. Schwehr, TAMUG (Co-PIs).	
Identification of Multiple Mercury Sources to Stream Sediments near Oak Ridge, TN, USA	63
Patrick Donovan (pmdon@umich.edu) - University of Michigan, Joel D. Blum (PI), Baohua Gu (ORNL); Jason D. Demers (U of Michigan) (Co-PIs).	
Illite spatial distribution regulates Cr(VI) adsorption capacity and kinetics	64
Li Wang (wangli2008ying@gmail.com) - Penn State University, Li Li (PI).	
<i>University-Led Research</i>.....	65
Induced Polarization Signature of Biofilms in Porous Media: From Laboratory Experiments to Theoretical Developments and Validation.....	65
Estella Atekwana (estella.atekwana@okstate.edu) - Oklahoma State University (PI), Marianna Patrauchan - Oklahoma State University; Andre Revil; Colorado School of Mines (Co-PIs).	
Isotopic Characterization of Biogeochemical Pools of Mercury and Determination of Reaction Pathways for Mercury Methylation	66
Joel Blum (jdblum@umich.edu) - Univ of Michigan, J Blum (PI), B Gu, ORNL; J Demers, Univ Mich; F He, ORNL; W Zheng, ORNL (Co-PIs).	
Reactivity of Iron-Bearing Phyllosilicates with Uranium and Chromium Through Redox Transition Zones	67
Bill Burgos (wdb3@psu.edu) - Penn State University (PI), Hailiang Dong, Miami University (Ohio) (Co-PIs).	
Inorganic Geochemical Controls on Neptunium Transport: Co-Precipitation in Minerals.....	68
Peter Burns (pburns@nd.edu) - University of Notre Dame(PI).	
Dominant Mechanisms of Uranium-Phosphate Reactions in Subsurface Sediments	69
Jeffrey Catalano (catalano@wustl.edu) - Washington University in St. Louis (PI), Daniel E. Giammar, Washington University in St. Louis; Zheming Wang, PNNL (Co-PIs).	

Uranium fate in acidic waste-weathered sediments: Scaling of molecular processes to predict reactive transport	70
Jon Chorover (chorover@cals.arizona.edu) - University of Arizona (PI), Peggy O'Day; Carl Steefel; Karl Mueller; Wooyong Um; John Zachara; Estela Reinoso-Maset; Nico Perdrial; Angelica Vazquez-Ortega; Masa Kanematsu (Co-PIs).	
Bacterial Nanowires and Extracellular Electron Transfer to Heavy Metals and Radionuclides by Bacterial Isolates from DOE Field Research Centers	71
Yuri Gorby (gorbyy@rpi.edu) - Rensselaer Polytechnic Institute (PI), Matthew Fields, Montana State University; Lauren Franco, Montana State University, Manfred Auer, Lawrence Berkeley National Lab; Edmond Leung, University of Southern California, and Shiue-Lin Li, University of Southern California (Co-PIs).	
Methods to Quantify Mercury Bioavailability in Sulfidic Sediments	72
Helen Hsu-Kim (hsukim@duke.edu) - Duke University, (PI).	
Fate of Uranium During Transport Across the Groundwater-Surface Water Interface	73
Peter Jaffe (jaffe@princeton.edu) - Princeton University (PI), H.S. Chang (Univ. Georgia), E. Gilson, (Princeton University), D.I. Kaplan, D. Li (SRNL), P. Koster van Groos (Princeton Univ.), A.D. Peacock (Microbial Insights), K. Scheckel (EPA), and John Seaman (Univ. Georgia) (Co-PIs).	
Integrated geophysical measurements for bioremediation monitoring: combining NMR, magnetic methods and SIP.	74
Kristina Keating (kmkeat@andromeda.rutgers.edu) - Rutgers University (PI), Rutgers University; Dimitris Ntarlagiannis, Rutgers University; Kenneth Williams, LBNL (Co-PIs).	
Identification of a c-type cytochrome involved in Mn(IV) reduction in Anaeromyxobacter dehalogenans strain 2CP-C	75
Frank Loeffler (frank.loeffler@utk.edu) - University of Tennessee & Oak Ridge National Laboratory (PI), Susan Pfiffner, University of Tennessee; Robert Hettich, Oak Ridge National Laboratory (Co-PIs).	
Going Wireless: Fe(III) Oxide Reduction without Pili by Geobacter sulfurreducens Strain JS-1.....	76
Derek Lovley (dlovley@microbio.umass.edu) - University of Massachusetts (PI).	
SMART (Subsurface Microbial Activity in Real Time) Technology for Real-Time Monitoring of Subsurface Microbial Metabolism.....	77
Derek Lovley (dlovley@microbio.umass.edu) - University of Massachusetts (PI).	
Radiocarbon Signature of Microbial DNA from a Reducing Zone of a Floodplain aquifer, Rifle Colorado.....	78
Brian Mailloux (bmaillou@barnard.edu) - Barnard College (PI); Alison Spodek Keimowitz (co-PI) - Vassar College; James F Ranville (co-PI), Valerie Stucker, Jonathan O. Sharp - Colorado School of Mines; Kenneth H. Williams - LBNL; Bruce Buchholz - LLNL.	
Real-time, on-site and quantitative detection of bioavailable radionuclides and heavy metals in contaminated water at DOE sites.....	79
Debapriya Mazumdar (pmazumdar@andalyze.com) - ANDalyze Inc., Yi Lu (PI), Yi Lu, University of Illinois Urbana Champaign - PI; Debapriya Mazumdar, ANDalyze Inc. Co-PI (Co-PIs).	
Strikingly Different Form of Organic Carbon in Soils of Temperate and Permafrost Soils: Implications for Carbon and Metal Cycling.....	80
Satish Myneni (smyneni@princeton.edu) - Princeton University (PI).	
Development of a Self-Consistent Model of Plutonium Sorption: Quantification of Sorption Enthalpy and Ligand-Promoted Dissolution	81

<p>Brian Powell (bpowell@clermson.edu) - Clemson University (PI), Daniel I. Kaplan, Savannah River National Laboratory; Yuji Arai, University of Illinois - Urbana Campaign; Udo Becker, University of Michigan; Rod Ewing, Standford University (Co-PIs).</p>	
<p>Using mercury-resistant bacteria to examine the effects of thiol complexation and thiol and Mer transporters on the microbial bioavailability of inorganic Hg and methylmercury</p>	82
<p>John Reinfelder (reinfelder@envsci.rutgers.edu) - Rutgers University, Nathan Yee (PI), Nathan Yee, Rutgers University; Tamar Barkay, Rutgers University (Co-PIs).</p>	
<p>Plutonium Immobilization and Mobilization by Soil Organic Matter.....</p>	83
<p>Peter H. Santschi (Santschi@tamug.edu) - Texas A&M University (PI), Kathleen A. Schwehr, Chen Xu, Matthew Athon, Yi-Fang Ho, ; 2Patrick G. Hatcher, Nichole Didonato; 3Daniel I. Kaplan (Co-PIs). 1Department of Marine Sciences, Texas A&M Univ.; 2Department of Chemistry & Biochemistry, College of Sciences, Old Dominion University; 3 Savannah River National Laboratory.</p>	
<p>Collaborative Research: The Importance of Organo-Iodine and Iodate in Iodine-127,129 Speciation, Mobility, and Microbial Activity in Groundwater at DOE Sites</p>	84
<p>Peter H. Santschi (santschi@tamug.edu) - Texas A&M University (PI), Kathleen A. Schwehr, Saijin Zhang, Chen Xu, Hsiu-Ping Li, Yi-Fang Ho, and Russell Grandbois (Texas A&M Univ.-Galveston); Daniel Kaplan and Kimberly A. Roberts (SRNL), and Chris M. Yeager (LANL) (Co-PIs).</p>	
<p>A comparison of Hg(II) uptake and accumulation between mercury methylating and non-methylating bacteria</p>	85
<p>Jeffra Schaefer (jschaefer@envsci.rutgers.edu) - Rutgers University (PI), Francois M. M. Morel; Department of Geosciences; Princeton University (Co-PIs).</p>	
<p>Electron Transfer and Atom Exchange Between Fe(II) and Structural Fe(III) in Clays</p>	86
<p>Michelle Scherer (michelle-scherer@uiowa.edu) - University of Iowa (PI), Kevin M. Rosso PNNL; Brian L. Beard and Clark M. Johnson U. Wisconsin; Maxim I. Boyanov, Kenneth M. Kemner, and Edward J. O'Loughlin ANL (Co-PIs).</p>	
<p>Geochemical zonation linked to microbial spatial distribution and microbe-mineral interactions in metal-immobilizing systems</p>	87
<p>Jonathan (Josh) Sharp (jsharp@mines.edu) - Colorado School of Mines (PI), S.M. Webb and J.R. Bargar - Stanford Synchrotron Radiation Lightsource (Co-PIs).</p>	
<p>238U/235U as an indicator of re-oxidation of U(IV) in the subsurface of remediated sites.....</p>	88
<p>Alyssa Shiel (ashiel@illinois.edu) - University of Illinois at Urbana-Champaign, Craig Lundstrom (PI), Thomas Johnson (University of Illinois at Urbana-Champaign) (Co-PIs).</p>	
<p>Identifying Components of Toxic Metal Stress and Hg Methylation with Global Proteomics</p>	89
<p>Anne Summers (summers@uga.edu) - University of Georgia (PI); Susan M. Miller, University of California-San Francisco; Mary S. Lipton, EMSL, Pacific Northwest National Laboratory; Judy Wall, University of Missouri-Columbia (Co-PIs).</p>	
<p>Mineral Solubility and Free Energy Controls on Microbial Reaction Kinetics: Application to Contaminant Transport in the Subsurface</p>	90
<p>Martial Taillefert (mtaillef@eas.gatech.edu) - Georgia Institute of Technology (PI), Philippe Van Cappellen, University of Waterloo; Carl Steefel, LBNL (Co-PIs).</p>	
<p>Survival During Long Term Starvation: Global Proteomics Analysis of Geobacter sulfurreducens Under Prolong Electron Acceptor and Donor Limitation.....</p>	91
<p>Ming Tien (mxt3@psu.edu) - Penn State University (PI), Susan Brantley, Penn State University (Co-PIs).</p>	
<p>Microbiological-enhanced mixing across scales during in-situ bioreduction of metals and radionuclides at Department of Energy Sites.....</p>	92

Albert Valocchi (valocchi@illinois.edu) - University of Illinois, (PI); Charles J. Werth; Wen-Tso Liu; Robert Sanford; (University of Illinois) (Co-PIs).

Long-term uranium sequestration as nitrate invades a previously reduced zone - DOE Oak Ridge IFRC site93

Weimin Wu (billwu@stanford.edu) - Stanford University, Craig S. Criddle (PI).

Hg(0) oxidation by Anaerobic Bacteria94

Nathan Yee (nyee@envsci.rutgers.edu) - Rutgers University (PI), John R. Reinfelder (Rutgers); Tamar Barkay (Rutgers) (Co-PIs).

TES Poster Abstracts95

Ameriflux95

Understanding Interannual Variability of Long Term Flux Measurements over Oak Savanna and Annual Grassland95

Dennis Baldocchi (baldocchi@berkeley.edu) - University of California, Berkeley (PI), Siyan Ma (co-author) (Co-Pi).

AmeriFlux Management Program QA/QC Technical Team96

Sebastien Biraud (scbiraud@lbl.gov) - Lawrence Berkeley National Laboratory (PI), Stephen Chan 1, Chad Hanson 2, David Billesbach 3, and Margaret Torn 1; 1: Lawrence Berkeley National Laboratory; 2: Oregon State University; 3: University of Nebraska, Lincoln (Co-PIs).

Connecting ecosystem carbon observatories in Europe and USA - the COPEUS project and the ICOS infrastructure97

Dario Papale (darpap@unitus.it) - ICOS ETC - University of Tuscia, Viterbo (ITALY), (PI).

AmeriFlux Data Collection, Processing, and Data User Support98

Gilberto Pastorello (gzpastorello@lbl.gov) - Lawrence Berkeley National Laboratory, Margaret Torn (PI), Deb Agarwal (project leader); Dario Papale; Cristina Poindexter; Boris Faybishenko; Tom Boden; (Co-PIs).

The AmeriFlux Management Project: Overview99

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

Early Career Awards 100

Model-data scaling approaches for assessing the pan-Arctic permafrost carbon feedback100

Daniel Hayes (hayesdj@ornl.gov) - ORNL (PI).

Methane Oxidation in Boreal Peatlands: A Joint Field, Laboratory and Modeling Investigation101

Rebecca Neumann (rbneum@u.washington.edu) - University of Washington (PI).

Federal Agency-Led Research 102

Quantifying the interactions between plant water uptake and hydraulic redistribution on the components of evapotranspiration in a mature, unmanaged forest stand102

A. Christopher Oishi (acoishi@fs.fed.us) - USDA Forest Service, Coweeta Hydrologic Laboratory, Jean-Christophe Domec (PI)- North Carolina State University & Duke University; John King- North Carolina State University; Asko Noormets- North Carolina State University; Ram Oren- Duke University.; Sari Palmroth- Duke University; Jennifer Swenson- Duke University (Co-PIs).

Climate feedbacks in drylands: linking carbon cycling and energy balance above- and belowground103

Sasha Reed (screed@usgs.gov) - US Geological Survey (PI), Anthony Darrouzet-Nardi USGS; Tom Painter Jet Propulsion Laboratory; Jayne Belnap USGS (Co-PIs).

Institute 104

Carbon Dynamics of Forest Recovery under a Changing Climate: Forcings, Feedbacks, and Implications for Earth System Modeling.....104

Kristina Anderson-Teixeira (teixeirak@si.edu) - Smithsonian (PI), Adam D. Miller, Smithsonian; Jennifer McGarvey, Smithsonian; Michael Dietze, Boston University; David LeBauer, University of Illinois; Benjamin D. Duval, USDA ARS; Evan H. DeLucia, University of Illinois (Co-PIs).

Solar Induced Fluorescence: Theory and Measurement Approaches 105

Joe Berry (jberry@carnegiescience.edu) - Carnegie Institution for Science (PI), Jung-Eun Lee, Brown Univ; Pierre Gentine, Columbia Univ; Benjamin Lintner, Rutgers Univ. (Co-PIs).

Hydraulic Redistribution of Water through Plant Roots and Implications for Carbon Cycling and Energy Flux at Multiple Scales 106

Zoe Cardon (zcardon@mbl.edu) - Marine Biological Laboratory (PI/Project leader); Rebecca Neumann, University of Washington; Guiling Wang, University of Connecticut; Daniel Gage, University of Connecticut (Co-PIs).

Large-scale shifts in land metabolic activity indicated by changing seasonal cycle of atmospheric CO₂ ... 107

Ralph Keeling (rkeeling@ucsd.edu) - Scripps Institution of Oceanography (PI).

Methane Emissions from Upland Trees 108

Scott Pitz (megoigalp@si.edu) - Smithsonian Environmental Research Center, Patrick Megoigal- Smithsonian Environmental Research Center (PI/ project leader); Lisa Schile- Smithsonian Environmental Research Center; Katalin Szlavecz- Johns Hopkins University (Co-PIs).

Partitioning Autotrophic and Heterotrophic Contributions to Soil Respiration: A Tale of Two Trenches 109

Kathleen Savage (savage@whrc.org) - The Woods Hole Research Center, Scott Saleska (PI), Eric Davidson; Rich Wehr- U of Arizona; Adrien Finzi- Boston U; Paul Moorecroft- Harvard U; (Co-PIs).

Physiological controls of stem respiration and soil respiration in a temperate forest..... 110

Jianwu Tang (jtang@mbl.edu) - MBL Ecosystems Center (PI).

NGEE-Artic 111

Development of reduced order models to capture subgrid-scale soil moisture dynamics in a polygonal tundra landscape..... 111

Gautam Bisht (gbisht@lbl.gov) - Lawrence Berkeley National Laboratory (PI), George S. H. Pau (LBL), William J. Riley (LBL) (Co-PIs).

Modeling controls on the decomposition of Soil Organic Matter 112

Dipankar Dwivedi (ddwivedi@lbl.gov) - LBL (PI), William J. Riley, Bardan Ghimire, Gautam Bisht, Jinyun Tang, Margaret S. Torn (Co-PIs).

NGEE Arctic: Biogeochemical controls on microbial CO₂ and CH₄ production in polygonal soils from the Barrow Environmental Observatory..... 113

David Graham (grahamde@ornl.gov) - Oak Ridge National Laboratory, Stan Wullschleger (ORNL) (PI), Taniya Roy Chowdhury (ORNL); Elizabeth Herndon (ORNL); Mallory Ladd (UT Knoxville); Dwayne Elias (ORNL); Tommy J. Phelps (ORNL/UT Knoxville); Baohua Gu (ORNL); Liyuan Liang (ORNL) (Co-PIs).

Biogeochemical processes affecting Arctic tundra soil organic matter degradation and greenhouse gas emission.....	114
Baohua Gu (gub1@ornl.gov) - Oak Ridge National Laboratory (PI); Elizabeth M. Herndon (ORNL); Benjamin F. Mann (ORNL); Taniya Roy Chowdhury (ORNL); John R. Bargar (SLAC); Stan Wullschleger (ORNL); David Graham (ORNL); Liyuan Liang (ORNL) (Co-PIs).	
Representativeness-Based Sampling Network Design and Scaling Strategies for Measurements in Arctic and Tropical Ecosystems	115
Forrest Hoffman (forrest@climatemodeling.org) - Oak Ridge National Laboratory, Stan Wullschleger (PI), Jitendra Kumar (ORNL), Zachary Langford (ORNL), Nathan Collier (ORNL), Victoria Sloan (ORNL), Richard T. Mills (Intel Corp.), William W. Hargrove (USDA Forest Service) (Co-PIs).	
The NGE Arctic Data Archive -- Portal for Archiving and Distributing Data and Documentation	116
Terri Killeffer (killefferts@ornl.gov) - ORNL, Tom Boden (ORNL) (PI), Giri Palanisamy (ORNL), Ranjeet Devarakonda (ORNL), Terri Killeffer (ORNL), Misha Krassovski (ORNL), Les Hook (ORNL) (Co-PIs).	
Multi-scale modeling of hydrologic and biogeochemical processes in Arctic ecosystems	117
Jitendra Kumar (jkumar@climatemodeling.org) - Oak Ridge National Laboratory (PI), Nathan Collier, ORNL; Fengming Yuan, ORNL; Guoping Tang, ORNL; Gautam Bisht, LBNL; Xiaofeng Xu, ORNL; Peter Thornton, ORNL (Co-PIs).	
Pan-arctic ice wedge degradation in continuous permafrost and hydrological implications	118
Anna Liljedahl (akliljedahl@alaska.edu) - University of Alaska Fairbanks ¹ , Stan Wullschleger (PI), Julia Boike ² , Ronald P. Daanen ³ , Gerald V. Frost ⁴ , Guido Grosse ² , Nadya Matveyeva ⁵ , Marius Necsoiu ⁶ , Martha K. Reynolds ⁷ , Vladimir Romanovsky ⁸ , Donald A. Walker ⁷ ; (Co-PIs).	
Use of Environmental Tracers for Multi-Scale Investigation of Hydrologic Mixing and Connectivity in the Arctic Coastal Plain, near Barrow, Alaska	119
Brent Newman (bnewman@lanl.gov) - Los Alamos National Laboratory (PI), Jeff Heikoop, Los Alamos National Laboratory; Cathy Wilson, Los Alamos National Laboratory; Stan Wullschleger, Oak Ridge National Laboratory & Project Leader (Co-PIs).	
Status of NGE-Arctic Track 2 Model Development: Incorporating Dynamic Topography in Fine-scale Models	120
Scott Painter (spainter@lanl.gov) - Los Alamos National Laboratory (PI), Ethan Coon (LANL); Markus Berndt (LANL); Rao Garimella (LANL); David Moulton (LANL); Cathy Wilson (LANL); Peter Thornton (ORNL) (Co-PIs).	
Three-phase models for thermal hydrology of frozen, variably saturated soils	121
Scott Painter (spainter@lanl.gov) - Los Alamos National Laboratory (PI), Satish Karra (Co-PIs).	
Photosynthesis, Earth System Models and the Arctic.....	122
Alistair Rogers (arogers@bnl.gov) - Brookhaven National Laboratory, Stan Wullschleger (PI), Rachel A. Wyatt, University of New Brunswick; Bryn M. Morgan, LANL; Victoria L. Sloan, ORNL; Chonggang Xu, LANL; Shawn Serbin, BNL; Nathan G. McDowell, LANL; David S. Kubien, University of New Brunswick; Richard J. Norby, ORNL; Stan D. Wullschleger, ORNL (Co-PIs).	
The role of lateral transport on storage and fate of soil carbon in permafrost dominated hillslopes and hollows.	123
Joel Rowland (jrowland@lanl.gov) - Los Alamos National Laboratory (PI), Eitan Shelef - Los Alamos National Laboratory; ; Cathy Wilson - Los Alamos National Laboratory (Co-PIs).	
Radiocarbon measurements to assess soil carbon vulnerability in Arctic coastal tundra	124
Lydia Smith (lydiaismith@lbl.gov) - University of California, Berkeley, Margaret Torn, Lawrence Berkeley National Laboratory (PI), Stan Wullschleger (Co-PIs).	

Metagenomics and microbial community profiling across polygon features at the Next Generation Ecosystem Experiment (NGEE)-Arctic Barrow site.....	125
Neslihan Tas (ntas@lbl.gov) - LBNL, Janet K. Jansson (PI), Margaret Torn, Lydia Smith, Shi Wang, Yuxin Wu, Craig Ulrich, Baptiste Dafflon, Timothy Kneafsey, David Graham, Susannah Tringe, Tanja Woyke, Susan Hubbard, Stan Wullschleger (Co-PIs).	
NGEE-Arctic: migrating knowledge across scales to improve climate prediction	126
Peter Thornton (thorntonpe@ornl.gov) - Oak Ridge National Laboratory, Stan Wullschleger (PI).	
Multi-scale Geophysical Studies at the NGEE-Arctic Site	127
Yuxin Wu (YWu3@lbl.gov) - Lawrence Berkeley National Lab, Stan D.Wullschleger (PI).	
Characterizing rooting depth distribution and nitrogen acquisition by dominant tundra plant species...128	
Stan Wullschleger (wullschlegsd@ornl.gov) - Oak Ridge National Laboratory (PI), Ingrid J. Slette, ORNL; Stan D. Wullschleger, ORNL; Colleen M. Iversen, ORNL; Victoria L. Sloan, ORNL; Joanne Childs, ORNL; Richard J. Norby, ORNL (Co-PIs).	
Scientific Focus Areas (SFA).....	129
Temporal, Spatial, and Uncertainty Aspects of Carbon Dioxide Emissions from Fossil Fuel Combustion: Highlights of the Last Two Years of TES Funding	129
Robert Andres (andresrj@ornl.gov) - ORNL, Paul Hanson (PI).	
Controls over biogenic volatile organic compounds from Amazon forests as part of GoAmazon	130
Jeffrey Chambers (jchambers@lbl.gov) – LBNL (PI), Kolby Jardine, LBNL; Jennifer Holm, LBNL; Ryan G. Knox, LBNL; Andrea Teixeira, LBNL; Jose F. de Goncalves, INPA; Niro Higuchi, INPA; Antonio Manzi, INPA; Margaret Torn, INPA (Co-PIs).	
Full-column Greenhouse Gas Profiles Measured at ARM SGP.....	131
Marc Fischer (mifischer@lbl.gov) – LBNL (PI), C. Sweeney, A. Karion, J. Higgs, T. Newberger, S. Wolter, S. Biraud, R. Chadwick, D. Wunch, P. Wennberg, P. Tans (Co-PIs).	
Vertical profiles of peat pore water chemistry in a northern peatland reveal dynamic element cycles ...132	
Natalie Griffiths (griffithsna@ornl.gov) - Oak Ridge National Laboratory (PI), Stephen D. Sebestyen, USDA Forest Service, Northern Research Station, Grand Rapids, MN (Co-PIs).	
Lack of explicit representation of mesophyll diffusion explains persistent overestimation of growth rates of historical atmospheric CO₂ by Earth System Models	133
Lianhong Gu (lianhong-gu@ornl.gov) - Oak Ridge National Laboratory (PI), Stephen G. Pallardy; University of Missouri (Co-PIs).	
ORNL's Terrestrial Ecosystem Science Scientific Focus Area -2014.....	134
Paul J. Hanson (hansonpj@ornl.gov) - Oak Ridge National Laboratory (PI), Daniel M. Ricciuto, ORNL; Peter E. Thornton, ORNL; Project Participants..... 134	
ORNL's TES SFA Data and Model Management and Archiving Facilitate Data Sharing and Model-Data Integration.....	135
Les Hook (hookla@ornl.gov) – ORNL (PI), Ranjeet Devarakonda [^] , Jeffery S. Riggs [*] , Misha B. Krassovski [^] , Paul J. Hanson [^] , and Thomas A. Boden [^] ; ; [^] Environmental Sciences and [*] Logistical Services Divisions, Oak Ridge National Laboratory (Co-PIs).	
Impact of fire and natural thaw on permafrost microbial ecology.....	136
Janet Jansson (jrjansson@lbl.gov) - LBNL (PI), Margaret Torn, LBNL; Mark Waldrop (USGS) ; Jenni Hultman (LBNL); Neslihan Tas (LBNL) (Co-PIs).	

Climatic and edaphic effects on root- and leaf-litter carbon inputs to temperate forest soils	137
Julie Jastrow (jdjastrow@anl.gov) - Argonne National Laboratory (PI), Roser Matamala, ANL ; Karis McFarlane, LLNL; Zhaosheng Fan, ANL; Rachel Porras, LBNL; Margaret Torn, LBNL; Tom Guilderson, LLNL; Paul Hanson, ORNL (Co-PIs).	
ANL Terrestrial Ecosystem Science SFA: Soil Carbon Response to Environmental Change.....	138
Julie Jastrow (jdjastrow@anl.gov) - Argonne National Laboratory (PI), Roser Matamala, ANL; Zhaosheng Fan, ANL; Umakant Mishra, ANL; Chien-Lu Ping, University of Alaska Fairbanks; Gary Michaelson, University of Alaska Fairbanks; Francisco Calderon, USDA-ARS; Vladimir Romanovsky, University of Alaska Fairbanks; Alexander Kholodov, University of Alaska Fairbanks (Co-PIs).	
Drought shifts internal carbon partitioning of recent photosynthates in black spruce trees: From bud to mature shoot	139
Anna Jensen (jensenam@ornl.gov) - ORNL, Jeffrey M Warren (PI) Environmental Sciences Division and Climate Change Science Institute, Oak Ridge National Laboratory.	
Functional unit testing of the Community Land Model at the PiTS-1 field experiment	140
Anthony King (kingaw@ornl.com) - Oak Ridge National Laboratory, Peter Thornton (PI), Dan Ricciuto, ORNL; Dali Wang, ORNL; Jeffrey Warren, ORNL (Co-PIs).	
Simulation of the Community Land Model in a pine stand with 13CO₂ and shading manipulations	141
Jiafu Mao (maoj@ornl.gov) - ORNL (PI).	
Differences in Biomass Distribution and Production Budgets between Cropland and Prairie Grassland..	142
Roser Matamala (matamala@anl.gov) - Argonne National Laboratory (PI), Zhaosheng Fan, ANL, Biosciences Division; David R. Cook, ANL, Environmental Science Division (Co-PIs).	
Microbial dormancy in terrestrial ecosystem models.....	143
Melanie Mayes (mayesma@ornl.gov) - ORNL (PI), Gangsheng Wang (ORNL); Sindhu Jagadamma (ORNL); Chris Schadt (ORNL) (Co-PIs).	
The effects of whole profile soil warming on decomposition of native soil carbon and 13C-labeled root inputs	144
Caitlin Pries (cehpries@lbl.gov) - Lawrence Berkeley National Laboratory, Margaret Torn (PI), Biao Zhu, John Curtis, Cristina Castanha, Rachel Porras, Don Herman (LBNL) (Co-PIs).	
Modeling the Hydrological dynamics of the SPRUCE S1 Bog.....	145
Daniel Ricciuto (ricciutodm@ornl.gov) - Oak Ridge National Laboratory, Peter Thornton (PI) (ORNL), Xiaoying Shi (ORNL); Jiafu Mao (ORNL); Paul Hanson (ORNL); Steve Sebestyen (USFS); Natalie Griffiths (ORNL); (Co-PIs).	
Scoping potential microbial responses to warming and drying in the SPRUCE peatland ecosystem.	146
Christopher Schadt (schadtcw@ornl.gov) - Oak Ridge National Laboratory, Paul J. Hanson (PI), J. Megan Steinweg (University of Wisconsin - Baraboo/Sauk County); Michael S. Robeson; Zamin K. Yang; Joel E. Kostka (Georgia Tech) (Co-PIs).	
LBNL Terrestrial Ecosystem Science SFA: Belowground carbon cycling	147
Margaret Torn (mstorn@lbl.gov) - Lawrence Berkeley National Laboratory (PI), Caitlin Hicks Pries - LBNL; Biao Zhu - LBNL; William Riley - LBNL; Eoin Brodie - LBNL; Janet Jansson -LBNL; Peter Nico - LBNL (Co-PIs).	
Vegetation turnover and nitrogen feedback drive temperate forest carbon sequestration in response to elevated CO₂. A multi-model analysis.....	148
Anthony Walker (alp@ornl.gov) - ORNL, Richard Norby (PI).	
Microbial dormancy in terrestrial ecosystem models.....	149
Gangsheng Wang (wanggg@ornl.gov) - Oak Ridge National Laboratory, (PI).	

Experiment-inspired Software Design and Ecosystem Modular Testing for CLM Development.....	150
Dali Wang (wangd@ornl.gov) – ORNL (PI), Y. Xu, University of Tennessee; J. Schuchart, Dresden University of Technology; T. Janjusic, National Center for Computational Science; F. Winkler, National Center for Computational Center; P. Thornton, Climate Change Science Institute; A. King, Climate Change Science Institute; L. Gu, Climate Change Science Institute (Co-Pis).	
Plant water relations in an ombrotrophic bog (SPRUCE S1) - partitioning water use and stress tolerance among components	151
Jeff Warren (warrenjm@ornl.gov) - Oak Ridge National Laboratory (PI), Joanne Childs, ORNL; David Weston, ORNL; Anna M. Jensen, ORNL; Stan D. Wullschlegler, ORNL (Co-Pis).	
Integrating In-situ Data with a Model for Examining Community-level CO₂ and CH₄ flux in a Carbon-rich Peatland in Northern Minnesota	152
Xiaofeng Xu (xux4@ornl.gov) - Oak Ridge National Laboratory (PI), Paul J. Hanson, Daniel Ricciuto, Jana R. Phillips, Xiaoying Shi, Jeffery S. Riggs, Colleen M. Iversen, David J. Weston, L.A. Hook, and Peter E. Thornton; Climate Change Science Institute and Environmental Sciences Division, ORNL (Co-Pis).	
The Genetic Potential of Microbial Depolymerization of SPRUCE Peatland in Marcell Experimental Forest, MN	153
Fan Yang (fyang@iastate.edu) - Iowa State University, Kirsten S. Hofmockel (PI), Erik A. Hobbie-University of New Hampshire (Co-Pis).	
Nutrient regulation of tropical ecosystem responses to environmental changes: a case study in the Amazon region	154
Xiaojuan Yang (yangx2@ornl.gov) - Oak Ridge National Lab, (PI).	
<i>Student Abstracts</i>	155
Seasonality of C allocation to roots in a mid-latitude forest	155
Rose Abramoff (rza@bu.edu) - Boston University, Scott R. Saleska - University of Arizona - project leader (PI), Richard Andrew Wehr - University of Arizona, Adrien C. Finzi - Boston University, Paul R. Moorcroft - Harvard University, J. William Munger - Harvard University, Eric A. Davidson - Woods Hole Research Center, Kathleen E. Savage - Woods Hole Research Center (Co-Pis).	
Annual balances of CO₂ and CH₄ from drained agricultural peatlands and restored wetlands in the Sacramento-San Joaquin Delta, California	156
Sara Knox (saraknox@berkeley.edu) - University of California, Berkeley, Dennis Baldocchi (PI).	
Investigating the impact of the widespread differential mortality of Pinus-edulus in piñon juniper woodlands: informing remote sensing with eddy-covariance.....	157
Dan Krofcheck (Krofcheck@Gmail.com) - University of New Mexico, Marcy Litvak (PI), Nate Mcdowell, LANL; Robert Sinsabaugh, UNM Biology; Andrew Fox, NCAR (Co-Pis).	
Divergence in how roots and mycorrhizae affect microbial decomposition	158
Jessica Moore (jessica.am.bryant@gmail.com) - University of Tennessee, Aimee Classen (PI), Melanie Mayes, Oak Ridge National Laboratory (Co-Pis).	
Variation in Microbial Processes Controlling Carbon Mineralization within Wetland Soils	159
Michael Schaefer (mvschae@stanford.edu) - Stanford University; Scott Fendorf, Stanford - Project Leader (PI); Marco Keiluweit, Stanford; Morris Jones, Stanford; Sharon Bone, SSRL; John Bargar, SSRL; Scott Fendorf, (Co-Pis).	
<i>TES Lab Research</i>	160
Pore- to Core-Scale Research to Inform Ecosystem-Scale Soil C Biogeochemistry.....	160

Vanessa Bailey (vanessa.bailey@pnnl.gov) - Pacific Northwest National Laboratory (PI), Ben Bond-Lamberty; Chongxuan Liu (Co-PIs).

Multiscale Simulations of Hydrological and Biogeochemical Processes from the Pore to Ecosystem Scales.....161

Chongxuan Liu (chongxuan.liu@pnnl.gov) - Pacific Northwest National Laboratory (PI), Ben Bond-Lamberty; Vanessa Bailey (Co-PIs).

Woodland mortality in a long-term drought experiment162

Nate McDowell (mcdowell@lanl.gov) - LANL (PI), Sanna Sevanto; Will Pockman (Co-PIs).

Functioning of wetlands as a source of atmospheric methane: a multi-scale and multi-disciplinary approach at SPRUCE.....163

Jennifer Pett-Ridge (pettridge2@llnl.gov) - Lawrence Livermore National Lab, Karis McFarlane (PI), Xavier Mayali-LLNL; Mike Singleton-LLNL; Ate Visser-LLNL; Brad Esser-LLNL; Tom Guilderson-LLNL (Co-PIs).

Differences in hydraulic strategy show in plant responses to heat and drought treatments.....164

Sanna Sevanto (sanna@lanl.gov) - Los Alamos National Laboratory, Nate McDowell (PI) (project leader); Chonggang Xu (Co-PIs).

University-Led Research.....165

Optimizing ground-penetrating radar for measurement of coarse root biomass and its application in determining elevated CO₂ legacy effects in an 11-year Florida experiment.....165

John Bain (johncbain@gmail.com) - Old Dominion University, Frank P. Day (PI) (project leader) - Old Dominion University; John R. Butnor, USDA Forest Service (Co-PIs).

Changes in Soil Microbial Community Structure and Function in a Chronosequence of Warming Experiments at Harvard Forest166

Jeffrey Blanchard (jeffb@bio.umass.edu) - University of Massachusetts (PI), Kristen DeAngelis, University of Massachusetts Amherst; Jerry Melillo, Marine Biological Laboratories (Co-PIs).

Multi-scale carbon cycle observations and ecosystem process modeling at Niwot Ridge, Colorado.....167

David Bowling (david.bowling@utah.edu) - University of Utah (PI); Charles Koven, LBNL; Britton Stephens, NCAR; Mark Williams, U. Colorado (Co-PIs).

Quantifying the role of topographical and edaphic complexity on coupled energy, water, and carbon cycles in forested, montane ecosystems168

Paul Brooks (pbrooks@email.arizona.edu) - University of Arizona, Holly Barnard² (PI), Hallie R. Adams², Erin Berryman^{2,3}, Margaret Burns², Erika L. Gallo¹, Clare Stielsra¹, and Tyson Swetnam¹; (Co-PIs). ¹University of Arizona; ²University of Colorado-Boulder; ³Colorado State University.

Towards the development of field methods to characterize environmental controls on rhizosphere priming effects169

Edward Brzostek (edbrzost@indiana.edu) - Indiana University, Jeffrey Dukes (PI), Richard Phillips, Indiana University (Co-PIs).

Improving Land-Surface Modeling of Evapotranspiration Processes in Tropical Forests170

Tony Cahill (tcahill@civil.tamu.edu) - Texas A&M University, Gretchen Miller (PI); Georgianne Moore (Co-PIs).

Large variability in ecosystem models explains a critical parameter for quantifying GPP with carbonyl sulfide.....171

Elliott Campbell (ecampbell3@ucmerced.edu) - UC Merced, John Campbell (PI), Ulrike Seibt, UCLA; Joe Berry, Carnegie; Margaret Torn, LBNL; David Billesbach, U Nebraska (Co-PIs).

Incorporating below ground biology and soil physical properties into a soil carbon degradation model through experimenting across ecotypes	172
Aimee Classen (atclassen@gmail.com) - University of Tennessee & The University of Copenhagen (PI), Melanie Mayes ORNL (Co-PIs).	
Confronting models with regional CO₂ observations to improve interpretation of drought stress and emissions (anthropogenic and fire).....	173
James Ehleringer (jim.ehleringer@utah.edu) - University of Utah (PI), John Lin, Utah; Britt Stephens, NCAR; Peter Thonrton, ORNL; Robert Andres, ORNL; (Co-PIs).	
Nutrient Cycle Impacts on Forest Ecosystem Carbon Cycling	174
Joshua Fisher (joshbfisher@gmail.com) - UCLA (PI), Richard Phillips, Tom Evans (Indiana University) (Co-PIs).	
Climate change alters woody shrub carbon storage and utilization in a moist acidic tundra.....	175
Charles Flower (cflowe3@uic.edu) - University of Illinois at Chicago, Miquel Gonzalez-Meler and Jeffery Welker (PI).	
Effects of Regional Groundwater on Tropical Rainforest Streams: Carbon Degassing and Particulate Organic Matter.....	176
David Genereux (genereux@ncsu.edu) - North Carolina State University (PI), Dr. Christopher L. Osburn, North Carolina State University; Dr. Steven F. Oberbauer, Florida International University; Dr. Diana Oviedo-Vargas, North Carolina State University (Co-PIs).	
Carbon and water cycling following low-severity disturbance in an Upper Great Lakes forest: Empirical and modeling results from an AmeriFlux core site	177
Christopher Gough (cmgough@vcu.edu) - Virginia Commonwealth University; Peter Curtis (PI); Gil Bohrer, Ohio State University; Knute Nadelhoffer, University of Michigan (Co-PIs).	
Carbon Dynamics of the Greater Everglades Watershed and Implications of Climate Change	178
Ross Hinkle (rhinkle@ucf.edu) - University of Central Florida (PI), Brian Benscoter and Xavier Comas, Florida Atlantic University; David Sumner and Don DeAngelos, United States Geological Survey (Co-PIs).	
Spatial patterns and source attribution of CH₄ emissions in an urban airshed to regional/global methane budgets	179
Francesca Hopkins (fhopkins@uci.edu) - Dept. of Earth System Science, UC Irvine, Project leader: James Ehleringer, University of Utah; co-PI: James Randerson, University of California Irvine; co-PI: Chun-Ta Lai, San Diego State University.	
Constraining the simultaneous effects of elevated CO₂, temperature, and shifts in rainfall patterns on ecosystem carbon fluxes using multi-scale resource optimization theories.....	180
Gabriel Katul (gaby@duke.edu) - Duke University (PI), Stefano Manzoni (Duke University & Swedish University of Agricultural Sciences); Daniele Way (Duke University & University of Western Ontario); Amilcare Porporato (Duke University); Sari Palmroth (Duke University); Ram Oren (Duke University) (Co-PIs).	
Coupling Peat Decomposition and Metagenomics to Incorporate Molecular Scale Processes into Climate Models	181
Joel Kostka (joel.kostka@biology.gatech.edu) - Georgia Institute of Technology (PI), Jeff Chanton, FSU; Bill Cooper, FSU; Chris Schadt, ORNL (Co-PIs).	
Coupled active and passive remote sensing to describe the land surface of piñon-juniper ecosystems ..	182
Dan Krofcheck (krofcheck@gmail.com) - UNM, Marcy Litvak (PI), Andrew Fox, NEON; Nate McDowell, LANL; Robert Sinsabaugh, UNM (Co-PIs).	
Responses of subalpine tree recruitment to warming within and above current altitudinal ranges.....	183

Lara Kueppers (lkueppers@ucmerced.edu) - UC Merced & LBNL (PI), Cristina Castanha^{1,2}, Andrew B. Moyes¹, Brynne Lazarus³, Erin Conlisk⁴, Matthew Germino³, Margaret S. Torn^{2,4}, John Harte⁴ and Jeffrey Mitton⁵ (Co-PIs). (1) University of California, Merced, (2) Lawrence Berkeley National Laboratory, (3) US Geological Survey, (4) University of California, Berkeley, (5) University of Colorado

The effects of climate, forest age, and disturbance history on carbon and water processes at AmeriFlux sites across gradients in Pacific Northwest forests184

Beverly Law (bev.law@oregonstate.edu) - Oregon State University (PI), Christoph Thomas (Co-PIs).

Collaborative Research on Ecophysiological controls on Amazonian precipitation seasonality and variability.....185

Jung-Eun Lee (leeje@brown.edu) - Brown University (PI), Joseph Berry, Carnegie Institution of Science; Pierre Gentine, Columbia University; Benjamin Lintner, Rutgers University (Co-PIs).

Evaluation and Improvement of Terrestrial Carbon Cycle Models With Observations.....186

Yiqi Luo (yluo@ou.edu) - University of Oklahoma (PI).

Control of Sphagnum-Derived Dissolved Organic Matter on Methane Production in Peatland Soils187

Cassandra Medvedeff (medvedef@chapman.edu) - School of Earth and Environmental Sciences, Chapman University, Scott Bridgham (PI), Jason K. Keller, School of Earth and Environmental Sciences, Chapman University (Co-PIs).

Fluxes of CO₂, CH₄, CO, BVOCs, NO_x, and O₃, in an old growth Amazonian forest188

J William Munger (jwmunger@seas.harvard.edu) - Harvard, SEAS, Steve Wofsy (PI), Kenia Wiederman (Harvard SEAS); Matt Hayek (Harvard SEAS); Scott Saleska (Univ. of Arizona); Humberto da Rocha (Universidade de São Paulo); Luciana Rizzo (Universidade Federal de São Paulo) (Co-PIs).

Aquaporin-Mediated Reduction in Root Hydraulic Conductivity Impacts Whole Stand Water Use and Carbon Assimilation: Scaling and Modeling the Effect of Sea Level Rise from Roots to the Ecosystem....189

Asko Noormets (anoorme@ncsu.edu) - North Carolina State University, Jean-Christophe Domec (PI); John King; (Co-PIs).

How well do stomatal conductance models perform on closing plant carbon budgets? A test using seedlings grown under current and elevated air temperatures190

Ram Oren (ramoren@duke.edu) - Duke University, Gabriel Katul (Duke University)(PI), Stefano Manzoni (Duke University & Swedish University of Agricultural Sciences, Department of Crop Production Ecology); Daniele Way (Duke University & University of Western Ontario); Amilcare Porporato (Duke University); Sari Palmroth (Duke University); (Co-PIs).

On the complementary relationship between marginal nitrogen and water use efficiencies among *Pinus taeda* leaves grown under ambient and enriched CO₂ environments191

Sari Palmroth (sari.palmroth@duke.edu) - Duke University, Gabriel Katul (Duke University) (PI); Stefano Manzoni (Duke University, & Swedish University of Agricultural Sciences, Department of Crop Production Ecology); Daniele Way (Duke University & University of Western Ontario); Amilcare Porporato (Duke University); Ram Oren (Duke University) (Co-PIs).

Modeling complex ecosystem carbon-nitrogen cycle dynamics after disturbance.....192

Anthony Parolari (ap263@duke.edu) - Duke University, Gabriel Katul (Duke University)(PI); Stefano Manzoni (Duke University & Swedish University of Agricultural Sciences, Department of Crop Production Ecology); Daniele Way (Duke University & University of Western Ontario); 4. Amilcare Porporato (Duke University); 5. Sari Palmroth (Duke University); 6. Ram Oren (Duke University) (Co-PIs).

Effects of disturbance on carbon sequestration in the New Jersey Pine Barrens193

Heidi Renninger (hrenninger@gmail.com) - Rutgers University; Karina Schafer - Rutgers University (PI); Gil Bohrer - Ohio State University; Kenneth Clark - USDA Forest Service; Nick Skowronski - USDA Forest Service (Co-PIs).

Interactive effects of climate change and decomposer communities on the stabilization of wood-derived carbon in soils: Catalyst for a new study194

Sigrid Resh (scresh@mtu.edu) - Michigan Technological University (PI), Evan Kane (Michigan Tech); Dana Richter (Michigan Tech) (Co-PIs).

Determining the Drivers of Redox Sensitive Biogeochemistry in Humid Tropical Forests..... 195

Leilei Ruan (ruanleil@msu.edu) - UC Berkeley, Whendee L. Silver UC Berkeley (PI), Peter Thornton Oak Ridge National Laboratory (Co-PIs).

Isotopic Partitioning of CO₂ fluxes revises understanding of mechanisms of forest carbon sequestration..... 196

Scott Saleska (saleska@email.arizona.edu) - University of Arizona (PI), Adrien Finzi, Boston University; Paul Moorcroft, Harvard University; Eric Davidson, Woods Hole Research Center; Rick Wehr, University of Arizona; William Munger, Harvard University (Co-PIs).

Tower-mounted cameras validate remotely sensed “green-up” of Amazon forest photosynthesis and reveal mechanisms underlying the seasonality of tropical forest metabolism..... 197

Scott Saleska (saleska@email.arizona.edu) - University of Arizona, Dennis Dye (PI), Scott Saleska, University of Arizona; Valeriy Ivanov, University of Michigan; Bruce Nelson, INPA, Brazil; Luiz Aragao, INPE, Brazil; Marciel Ferreira, Federal University of Amazonas, Brazil (Co-PIs).

The Impact of Permafrost Carbon Loss on the Carbon Balance of an Experimentally Warmed Tundra Ecosystem..... 198

Ted Schuur (tschuur@ufl.edu) - University of Florida (PI), Sue Natali, Woods Hole Research Center; Elizabeth Webb 1; Verity Salmon 1; Marguerite Mauritz 1; Rosvel Bracho 1; Christina Schaedel 1; Jack Hutchings 1; Grace Crummer 1; Caitlin Pries, Lawrence Berkeley Lab; Elaine Pegoraro 1 (Co-PIs). 1: University of Florida

Multi-scale methane fluxes from Howland Forest: merging tower and chamber flux measurements. 199

Julie Shoemaker (jshoemak@fas.harvard.edu) - Harvard University, Andrew Richardson (PI), David Hollinger, USDA forest service; Kathleen Savage, Woods Hole Research Center; Holly Hughes, Woods Hole Research Center (Co-PIs).

Developing surface-modified polymeric probes for the in-situ capture of plant root exudates..... 200

Nishanth Tharayil (ntharay@clemson.edu) - Clemson University (PI).

Up-rooting surface-atmosphere exchange models: How mycorrhizal associations may affect soil emission profiles 201

Amy Trowbridge (amtrowbr@indiana.edu) - Indiana University (PI), Paul C. Stoy; Montana State University; Richard P. Phillips; Indiana University (Co-PIs).

A New Approach to Synthesizing Results from Global Change Experiments..... 202

Kees Jan van Groenigen (cjangroenigen@nau.edu) - Northern Arizona University, Bruce Hungate (PI).

Advancing our understanding of carbon-climate feedbacks in Arctic tundra: litter input controls on soil organic matter turnover and formation 203

Matthew Wallenstein (matthew.wallenstein@colostate.edu) - Colorado State University (PI), Richard Conant, CSU; Francesca Cotrufo, CSU; Eldor Paul, CSU; Bill Riley, DOE; Jinyun Tang, DOE (Co-PIs).

Partitioning Ecosystem Canopy Transpiration to Evaluate the Sensitivity Stomatal Conductance to Changing Climate Indicators. 204

Eric Ward (ejward3@ncsu.edu) - North Carolina State University, Jean-Christophe Domec (PI), John King and Asko Noormets, North Carolina State University (Co-PIs).

The Prairie Heating and CO₂ Enrichment (PHACE) experiment: Synthesizing 8 years of data 205

David Williams (dgv@uwyo.edu) - University of Wyoming, Elise Pendall, University of Wyoming (PI/project leader); Kiona Ogle, Arizona State University; Jack Morgan, USDA-ARS; Bill Parton, Colorado State University; Dave Williams, University of Wyoming (Co-PIs).

EMSL Poster Abstracts	206
Subsurface Conditions Controlling Uranium Retention Pathways.....	206
Scott Fendorf (fendorf@stanford.edu) - Stanford University (PI), Michael Massey, Stanford University; Morris E. Jones, Stanford University; Juan Lezama, Stanford University; Gabrielle Dublet, Stanford University; Gordon E. Brown, Jr., Stanford University; Peter Nico, LBNL; Eugene Ilton, PNNL (Co-PIs).	
EMSL: A DOE Scientific User Facility for Terrestrial and Subsurface Science Research	207
Nancy Hess (nancy.hess@pnnl.gov) - EMSL (PI), Karl Mueller EMSL (Co-PIs).	
Pore-Scale and Continuum Simulation of Microfluidics Experiments on Reactive Transport and Multiphase Flow conducted at EMSL.....	208
Albert Valocchi (valocchi@illinois.edu) - University of Illinois, (PI), Charles J. Werth, Youneng Tang, Tory Boyd; University of Illinois at Urbana-Champaign; Haihu Liu; University of Strathclyde; Hongkyu Yoon; Sandia National Laboratory; Mart Oostrom; Tom Wietsma; Pacific Northwest National Laboratory; Changyong Zhang; Exxon-Mobil; (Co-PIs).	
Other Poster Abstracts.....	209
The DOE Joint Genome Institute--Advancing Energy & Environmental Science	209
Dan Drell (daniel.drell@science.doe.gov) DOE, Eddy Rubin Lawrence Berkeley National Laboratory (PI).	
Omics and Geochemistry: the ENIGMA 100-Well Survey.....	210
Terry Hazen (tchazen@utk.edu) - University of Tennessee, Knoxville (PI).	
Evaluating the ACASA model as a tool for flux interpretation at 4 AmeriFlux Sites.....	211
Jessica Osuna (osuna2@llnl.gov) - Lawrence Livermore National Laboratory, Sonia Wharton (LLNL) (PI), J. Osuna (LLNL), R.D. Pyles (UC-Davis), M. Falk (UC-Davis), S. Ma (UC-Berkeley), D. Baldocchi (UC-Berkeley), K. Bible (U-Washington), S. Biraud (LBNL) (Co-PIs).	
Progress toward developing a novel mini tunable diode laser for measuring CO₂ fluxes in situ	212
Jessica Osuna (osuna2@llnl.gov) - Lawrence Livermore National Laboratory (PI), Mihail Bora, LLNL (Co-PIs).	
Predictive Assimilation Framework for Subsurface Process Prediction.	213
Roelof Versteeg (roelof.versteeg@subsurfaceinsights.com) - Subsurface Insights (PI).	

SBR Poster Abstracts

Early Career Awards

Multi-system Analysis of Microbial Biofilms

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The majority of microorganisms in natural and engineered environments live in structured communities such as biofilms. Biofilms are comprised of microbial cells and a poorly characterized organic matrix commonly referred to as extracellular polymeric substance (EPS) that may support microbial interactions and biogeochemical reactions including extracellular electron transfer. Using high-resolution electron microscopy (EM) imaging, we have shown copious amounts of highly hydrated bacterial EPS are produced during microbial metal reduction. The co-location of extracellular electron transfer proteins and nanoparticulate reduced metal suggested that EPS played a key role in metal capture and precipitation.

Here we present a multi-faceted approach to determine the composition of biofilm EPS using synchrotron-based X-ray and infrared (IR) microimaging techniques combined with mass spectrometry imaging and high-resolution EM at the Environmental Molecular Sciences Laboratory. The result is a spatially resolved, complex chemical imaging of a biofilm community. X-ray microtomography produced images of hydrated biofilms to reveal the complex microstructure within a biofilm. Contrasting agents enhanced biofilm visibility at the high energies used. To investigate the micrometer- to nanometer-scale chemical signatures of biofilms, a cryo-sample preparation technique produced ultrathin biofilm sections for scanning transmission x-ray microscopy (STXM) and synchrotron IR microimaging. In STXM studies, we mapped the unique carbon signatures of biological molecules and found distinct differences between the cell surface and the EPS matrix. Concurrent with these studies, we used IR microimaging to produce high-megapixel datasets with IR spectral data showing the locations of key biofilm components (i.e., proteins, sugars, flavins, nucleic acids, lipids). The spatially resolved IR results were corroborated with bulk IR chemical data using chemically fractionated regions of biofilms.

In situ imaging was conducted using a novel microfluidic reactor for biofilm growth, confocal laser scanning microscopy analysis, and hydrated-state, time-of-flight secondary ion mass spectrometry imaging. We generated high-resolution two-dimensional chemical images of biofilms at their surface attachment interface and detected characteristic fatty acid fragments from microfluidic reactor-grown biofilms. These fatty acid fragments are being investigated as key factors for how biofilms attach to a surface in a microfluidic reactor.

The integration of the multiscale structural studies and in situ imaging of hydrated biofilms 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).

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

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Subsurface environmental systems are open and complex, in which intricate bio-hydro-geochemical processes interact across multiple spatial and temporal scales. Predictions of the subsurface system are inherently uncertain, and uncertainty is one of the greatest obstacles in groundwater reactive transport modeling. The goal of this project is two-fold: (1) developing new computational and mathematical methods for quantification of predictive uncertainty, and (2) using the developed methods as the basis to develop new methods of experimental design and data collection for reduction of predictive uncertainty.

In the second year of the project, we have developed a computational Bayesian framework for uncertainty quantification. The framework considers various sources of uncertainty in data, model structures, model parameters, and driving forces (e.g., natural changes related to climate change and human-induced engineering remediation). The framework can be used to evaluate predictive uncertainty from these sources and to identify major uncertainty sources. Based on this framework, we have extended variance-decomposition-based sensitivity analysis from a single model/scenario to the context of multi-models/scenarios. This is necessary to reliable selection of influencing model parameters and components, because parameter sensitivity may vary between models and/or scenarios. The Bayesian framework has been evaluated using a synthetic modeling that considers three scenarios of precipitation (due to climate change), two models that convert precipitation to recharge, and four parameters of groundwater flow and reactive transport. We have demonstrated that a large amount of computational cost can be saved by using the sparse-grid methods to implement numerical calculation of the framework. The framework will be used for the rest of the project for uncertainty quantification and reduction.

A number of insights have been gained through our numerical analysis for groundwater reactive transport modeling. We have shown that model residuals are non-Gaussian due to nonlinearity of biogeochemical reactions and coupling of flow, transport, and reaction processes. Using a more appropriate likelihood function can improve model prediction to reduce biasness in predictions and yield more accurate uncertainty quantification. For surface complexation models of uranium adsorption, we demonstrated that parametric uncertainty is caused by competing effects between different functional groups and between different reactions on a single functional group. This finding leads to the conclusion that effective and efficient uncertainty reduction can be achieved by designing column experiments that constrain the competing effects. In addition to the biogeochemical insights, we have also gained insights into numerical evaluation of marginal model likelihood function needed for quantification of model uncertainty.

Institute

¹⁵N and ¹⁸O Isotope Systematics of Anaerobic Abiotic Reduction of Nitrite by Iron (II)

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Evidence is mounting for the environmental importance of interactions between iron and nitrogen. While previous studies have shown that oxidation of Fe(II) by nitrate (NO₃⁻) and nitrite (NO₂⁻) - a reactive intermediate of both reductive and oxidative N cycling processes - the controls on these reactions in the environment remain poorly understood. Moreover, the N product of abiotic, anaerobic NO₂⁻ reduction by Fe(II) can include nitrous oxide (N₂O), nitric oxide, ammonium or dinitrogen gas - yielding a myriad of implications for the fate of N across all types of ecosystems. Furthermore, we posit that such reactions may represent an important control on the dual NO₃⁻ and NO₂⁻ isotopic composition in reducing environments low in organic carbon (e.g., aquifers). To date, however, the kinetic isotope effects (¹⁵ε and ¹⁸ε) of these processes remain uncharacterized and hence our ability to use the dual isotopic composition of these compounds as quantitative records of cycling processes remains limited.

Here we present the first investigation of the dual (¹⁵N and ¹⁸O) isotope systematics of abiotic nitrite reduction by Fe(II) minerals under a variety of environmentally relevant pH values (6 to 8) and reactant concentrations (200 μM nitrite; 1 to 10 mM Fe(II)). In our experiments, we observe rapid decreases in nitrite correlated with loss of Fe(II) and the precipitation of Fe minerals that were distinct among pH conditions. Further, we observed a distinct evolution in isotopic effect during experiments. During the early stages, nitrite reduction occurred with no isotope effect, while later isotope effects increased to 12-18‰ for both ¹⁵ε and ¹⁸ε, apparently reflecting an evolving importance of heterogeneous reactions with Fe(II) associated with minerals. Additionally, the degree of oxygen isotope exchange between water and nitrite also influenced results and was closely related to pH. Although no exchange occurred at pH 8, lower pH conditions slowed reaction rates and induced substantial exchange - effectively overprinting any kinetic isotope effect. Finally, although generally producing N₂, under certain conditions the reaction converted up to 40% of the nitrite to nitrous oxide - representing a potentially important abiotic source of this greenhouse gas under environmentally relevant conditions. As studies suggest the potential for anaerobic, abiotic nitrogen transformations coupled with iron cycling, the N and O isotope effects determined here will be helpful for using dual isotopes of nitrite (and nitrate) to decipher the biogeochemical fate of N in host of important environments including soils, sediments, wastewater treatment.

Scientific Focus Areas (SFA)

Interconnected Cycling of Fe, S, and C in the Terrestrial Subsurface: New Paths and Opportunities for Coupling Biotic and Abiotic Processes

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

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

In separate experiments, we investigate how the nature of organic C plays a critical role in determining the mechanism by which Fe(III) minerals are reduced. In microcosms containing both ferrihydrite and sulfate as electron acceptors and amended with acetate or lactate, we found that both acceptors were reduced simultaneously and that lactate promoted more rapid reduction. When glucose was used as the sole electron donor, however, ferrihydrite was reduced without a concomitant reduction of sulfate. The production of acetate per mol of glucose consumed differed between replicate bottles, as did the amount of total C recovered as organic acids, causing significant differences in the pH between the glucose-fed microcosms and variations in the total accumulation of aqueous Fe(II).

Because elements such as Fe, S, and C can cycle rapidly between different valence states in subsurface environments, actual pathways of electron flow are difficult to determine from geochemical measurements alone. By reconstructing the genomes of microorganisms that catalyze these processes from a metagenome, we can begin to unravel the metabolic networks active in these environments. We reconstructed the complete 2.4 Mb genome of a previously uncultivated epsilonproteobacterium by assembling short-read shotgun metagenomic data using a complexity reduction approach. Genomic evidence suggests that the organism is a chemolithoautotrophic diazotroph capable of deriving energy for growth by microaerophilic or nitrate-/nitric oxide-dependent oxidation of S(0), sulfide, sulfite, or H₂. At steady-state, these critical but transient metabolites often exist at only minute and difficult to measure concentrations, underscoring the critical role of genomic analysis in understanding the geochemistry of complex subsurface environments.

Characterizing Biogeochemical Hot Spots and Hot Moments in a Floodplain System

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Although spatially discrete biogeochemical hotspots and temporally restricted hot moments are known to account for a high percentage of nutrient cycling within terrestrial and aquatic ecosystems, the ability to effectively identify and incorporate them into reactive transport models remains a significant challenge. Using a combination of geophysical, solid and aqueous geochemical, hydrological, geological and microbiological datasets, and statistical techniques, we seek to identify relevant biogeochemical zonation and to quantify spatial and temporal variability of hydrological-biogeochemical properties across the Rifle floodplain. The zonation approach exploits the suppositions that: (1) many subsurface properties are likely to be correlated with each other; (2) some properties may exert a dominant control on biogeochemical cycling; and (3) some spatially extensive measurements (such as geophysical and remote sensing) may provide reasonable proxies for controlling variables, thus offering an approach to characterize zonation and key properties over large regions and in a minimally invasive manner. Once such zonation is identified, it can be used to parameterize the modeling domain as well as to guide characterization campaigns in a cost effective manner.

We develop and test our methods at the Rifle CO biogeochemical field study site as part of the LBNL Sustainable Systems SFA. Cluster analysis of all the datasets revealed the presence of several spatial zones across the site, which had unique distributions of geomorphic, hydrological, microbial, and geochemical properties. Using this method, we also identified and distributed biogeochemical hot spots, called naturally reduced zones, which are important regions for subsurface biogeochemical cycling. Furthermore, wavelet analysis was used to quantify the key controls on temporal variations in the geochemical data. Wavelet analysis results revealed that seasonal perturbations (~4 months) constitute hot moments that drive biogeochemical cycling at Rifle, with such activity confined to hot spots corresponding to the anthropogenically-contaminated zone. Interestingly, wavelets revealed a different dominant frequency (~3 months) for the naturally reduced zone at the Rifle site. The correspondence between biogeochemical zonation, seasonal variability, and other site-specific interactions from this study provide the characterization necessary for quantifying key controls at the Rifle site. Importantly, this zonation-based work is providing a framework for tractable yet sufficient parameterization of the LBNL SFA genome enabled reactive transport watershed simulator, GEWaSC.

Sustainable Systems SFA 2.0: Extensive Genome-Resolved Analyses Reveal Roles for Uncultivated Archaea and Bacteria in Subsurface Biogeochemical Cycling

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The subsurface is a vast reservoir of organic compounds and hosts a large fraction of microbial life, yet relatively little is known about sediment-associated and groundwater communities or their roles in carbon, nitrogen, sulfur and H₂ cycling. The Sustainable Systems Scientific Focus Area 2.0 (SFA) is investigating subsurface carbon biogeochemical cycling, and how these processes are impacted by changes in climate and land-use. The “Metabolic Potential” component is characterizing pathways in subsurface microbial communities to inform the central modeling effort of the SFA: Genome-Enabled Watershed Simulation Capability (GEWaSC). We have conducted deep metagenome sequencing of both unamended and acetate-stimulated sediment and groundwater samples from multiple depths and locations in an alluvial aquifer adjacent to the Colorado River, CO, USA. The genomic dataset comprises over 2.5 Tb of short-read Illumina sequences and three long-read Moleculo datasets. Notably, of the thousands of genomes recovered, almost all are novel at the genus-level or higher with little overlap in community membership across sample locations or matrix types. Many of the sampled archaea and bacteria are affiliated with phyla lacking cultivated representatives and some define previously unrecognized phyla. For example, we resolved three new archaeal phyla based on sequences from 111 newly sampled genomes and reconstructed two complete (finished) genomes. For bacteria, we sampled multiple new phylum-level lineages, reconstructed hundreds of draft genomes for two specific candidate phyla, recovered around two hundred near-complete genomes from across the bacterial domain, and finished twelve genomes. Based on genome size, we infer that many of the novel archaea and bacteria have ultrasmall cell size. Detailed metabolic analyses provided evidence for possible symbiotic lifestyles. The lack of recognizable respiratory pathways involved in sulfur, nitrogen, methane, oxygen or metal cycling suggests that the biogeochemical impact of these ultrasmall organisms is primarily associated with carbon fermentation and H₂ cycling. Metabolic predictions from the remaining members across all genomic datasets identify organisms possessing key traits such as nitrogen fixation, nitrate reduction, sulfur oxidation, H₂ production/consumption, degradation of refractory organic compounds and carbon fixation. This information, in combination with data regarding genome GC content, codon usage and genome size, constrain metabolic rates and define functional guilds as inputs to GEWaSC. Overall, our results have dramatically expanded genomic sampling of the microbial world, improved the taxonomic resolution of candidate phyla, and augmented understanding of metabolism within domains Archaea and Bacteria.

SLAC SFA: Coupled Cycling of Organic Matter, Uranium, and Biogeochemical Critical Elements in Subsurface Systems

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The ability to predict subsurface transport and fate of redox-active radionuclides, contaminants, and biogeochemical critical elements ("BCEs"², including C, N, S, and Fe) is hindered by a lack of knowledge of their speciation, reactivity, and biogeochemical pathways by which they are transformed. A growing body of evidence suggests that organic-rich sediments control the behavior of uranium and BCEs in contaminated floodplains at U.S. DOE legacy sites, particularly in the Western U.S. The stores of organic matter in these sediments fuel abundant microbial activity that converts organic carbon to CO₂ (via several intermediates) and transforms sulfate, iron, nitrate, and U(VI) to reduced species that drive further biogeochemical dynamics. Furthermore, in the presence of dissolved oxygen, microbial decomposition of organic nitrogen coupled to nitrification produces nitrate, a potent oxidant for U(IV) and other reduced species. The presence of NRZs and their attendant biogeochemical redox activity therefore are of intense interest for understanding and predicting radionuclide, metal, and BCE fate and transport.

The SLAC SFA is investigating biogeochemical redox processes that control subsurface uranium and BCE behavior in organic-rich fine-grained sediments common to river basins worldwide. We are using synchrotron, spectroscopic, microbial, stable isotope, electrochemical, and microscopy techniques, controlled laboratory experiments, and field sediments from multiple locations to obtain insights at a range of scales, from molecules and bacterial cells to river basins. Our project is providing process-level knowledge of globally significant BCE transformations, including natural organic matter, and uranium fate and transport in contaminated aquifers. These findings are helping to advance SRB modeling competencies at floodplain and regional scales.

SLAC SFA: Characterization of Uranium and Biogeochemical Critical Elements in Organic-Rich Sediments

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A growing body of evidence suggests that organic-rich sediments help to control the behavior of uranium and biogeochemical critical elements ("BCEs", including C, N, P, S, and Fe) in contaminated floodplains in Western U.S. DOE legacy sites. Lenses of these sediments containing also reduced uranium, iron, and sulfur, are referred to as naturally reduced zones (NRZs), and interact with groundwater along extensive interfaces. Large stores of organic matter in NRZs have the potential to fuel microbial activity and biogeochemical cycling of metals and BCEs. Consequently, NRZs are of intense interest as moderators of uranium and BCE fate and transport - locally at Rifle - and regionally in contaminated floodplains throughout the upper Colorado River basin. Understanding the molecular-scale speciation of uranium and BCEs is of central importance to advancing SBR predictive capabilities of NRZ-uranium-BCE-floodplain interactions. The mechanistic linkages between organic matter and uranium species are believed to be particularly important.

In the past year the SLAC SFA has investigated the following specific questions relating to NRZs at the Rifle site: (i) What is the molecular-scale speciation of U(IV), C, and N? (ii) What is the age of carbon in the aquifer and, by inference, the depositional age of the NRZs? Also, (iii) is carbon being exported to the surrounding aquifer? This work showed that non-crystalline U(IV) was the dominant form of uranium in all sediments examined. NRZ sediments were found to be surprisingly youthful, about 200 years old. N and C speciation in NRZs was found to be similar to that in the surrounding sediments, suggesting that NOM is being exported from the NRZs. Moreover, abundant proteinaceous coatings on NRZ minerals suggest the presence of bacterially-derived biomass. These observations contribute to the evolving picture of NRZs as youthful and biologically active zones that influence the surrounding aquifer.

Decomposition of thawing Arctic soil organic matter (SOM) is also of intense interest because it releases large amounts of methane and CO₂. Iron is believed to play a critical role in regulating bacterial metabolisms and hence the CO₂/methane balance. In collaboration with NGEE Arctic investigators, we used XAS to examine the speciation of Fe and SOM in samples from the Barrow Environmental Observatory. These measurements show that "dissolved" Fe(III) is present as both colloids and complexes, and different SOM functional groups are dominant in mineral soil vs dissolved fractions. These results are helping to build the molecular-scale basis for process-based modeling of SOM.

Uranium Biogeochemistry in Organic-Rich Sediments: Laboratory Analog Studies

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Zones of organic-rich reduced sediments at the Old Rifle, CO uranium ore processing site have been identified. These naturally reduced zones (NRZs) contain more than 100-fold higher U than ambient sediments and are perceived dominant contributors to uranium persistence in groundwater. Further, NRZs are likely regionally important to uranium plume persistence in the Colorado River Basin. The presence of natural organic matter (NOM) and low sediment permeability were concluded to be of central importance to the development of NRZs and their acquisition of uranium.

The SLAC SFA program seeks to elucidate the biogeochemical processes governing the formation, accumulation/reduction of uranium, and speciation of the biogeochemically active elements C, S, and Fe within NRZs. We have observed the formation of diffusion-limited reduced zones within artificial NRZ sediments, where the extent of reduction is governed by the NOM concentration and the spatial distribution of reduced zones by the sediment porosity. Further, we note that U(VI) is not strongly associated with particulate organic carbon and does not accumulate in sediments prior to the onset of reducing conditions. Subsequent to the onset of reduced conditions, U(IV) associates with particulate organic carbon, leading to the depletion of aqueous U. Additionally, U is not accumulated preferentially with any particular component of the biomass (inclusive of detrital plant residue). We are now exploring uranium distribution, speciation, and partitioning at varying U:OC ratios.

At low biomass levels, uraninite is a dominant product of U(VI) reduction. In order to assess the stability of authogenic uraninite, we have conducted long-term (21 month) oxidation studies of biogenic uraninite in Rifle wells. Our results indicate that uraninite can persist in suboxic aquifers for long periods of time (decades) in the absence of reducing conditions. Moreover, we show that Ca²⁺ bonds to uraninite surfaces with extremely high affinity, likely passivating it with respect to oxidation.

We are using a combination of approaches to characterize the distribution and speciation of C, S, Fe, and U in natural and simulated NRZs. In particular, we utilize x-ray absorption spectroscopy, micron-scale x-ray microprobe imaging, and scanning transmission x-ray microscopy (STXM) and nano-SIMS to determine the distribution and products of uranium reduction. This work will provide molecular-scale insights into the redox cycling of C, S, and Fe, and their implications for uranium behavior. Ultimately, this work will inform accurate descriptions of subsurface carbon, trace nutrient, and contaminant behavior in earth systems models.

Chemolithoautotrophy in the Rifle subsurface relevant to C, S, and Fe cycling

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The Sustainable Systems Scientific Focus Area (SFA) 2.0 aims to develop a predictive understanding of how climate-induced changes in hydrology and vegetation can affect overall watershed biogeochemical functioning. At the Rifle (CO) study site, this scope includes changes in water-table elevation due to reduced precipitation and recharge, and the resulting influx of dissolved oxygen (DO) 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 microbial communities and to use these data to inform the project's modeling effort (GEWaSC or Genome-Enabled Watershed Simulation Capability).

Although chemolitho(auto)trophic metabolism has not been extensively investigated in the subsurface several lines of evidence from early data in SFA 2.0 indicate that it can play a significant role in Rifle subsurface biogeochemistry. For example phylogenetic (16S rRNA) analyses of planktonic biomass collected during a DO release/perturbation experiment revealed the emergence of bacterial taxa known for their chemolithotrophic lifestyles [specifically Fe(II) and/or S oxidation] including *Sulfuricurvum* spp. (up to ~65% relative abundance) *Thiobacillus denitrificans* (up to ~25%) and *Gallionella* spp. (up to ~25%). In an analogous nitrate-release experiment Fe(II)-oxidizing *Gallionella* spp. were dominant in groundwater samples (14-50% throughout the study). Metagenome and metatranscriptome sequencing of DO and nitrate release samples is underway. Further evidence of chemolithoautotrophic metabolism in the Rifle subsurface came from shotgun metaproteomic analysis of background groundwater samples. Notably there was strong evidence for the activity of members of the order Gallionellales. Within each sample peptides matching more than 250 Gallionellales proteins were detected including RubisCO (for autotrophy). These findings are supported by metagenomic reconstructions from groundwater communities which revealed a broad diversity and abundance of RubisCO sequences from Archaea and Bacteria including form II RubisCO sequences most closely related to *Gallionella* and *Thiobacillus* spp. sequences. Based on results of the DO perturbation study and a recent non-SFA metatranscriptomic study by Methe and co-workers indicating the possible importance of the obligately chemolithoautotrophic S- and Fe(II)-oxidizing bacterium *Thiobacillus denitrificans* in the Rifle subsurface we isolated and sequenced two strains of *T. denitrificans* from Rifle groundwater. Comparisons of 46 selected genes associated with S oxidation CO₂ fixation (form I and II RubisCO) denitrification H₂ oxidation and U(IV) oxidation in these Rifle strains relative to a well-characterized soil-derived strain (ATCC 25259) revealed a very high level of synteny and protein sequence identity (mean =97%).

Microbial Sorption of Plutonium and the Role of Extracellular Polymeric Substances

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Decades of nuclear weapons testing and production have left a legacy of radionuclide contamination at many sites around the world. One of the most pressing concerns is the eventual fate of the radionuclides released into the environment. Plutonium (Pu) is of particular concern as over 2000 metric tons have been deposited in the subsurface worldwide. Its long half-life (^{239}Pu - 2.4×10^4 yr) coupled with high toxicity makes it of concern for long-term risk assessments. Complications in predicting environmental behavior of Pu arise from its ability to exist in different oxidation states (III, IV, V, and VI) and the resulting differences in geochemical behavior. Additional complexities in Pu behavior occur in the presence of microbes and microbial exudates.

We examined the sorption of Pu (IV) and Pu(V) to an aerobic bacterium *Pseudomonas* sp, isolated from Pu-contaminated groundwater collected at the Nevada National Security Site (Nevada, USA). To quantify the contribution of extracellular polymeric substances (EPS) to Pu sorption, we compared Pu sorption using cells with and without bound-EPS. Our results showed that while bound-EPS contributes significantly to Pu(V) sorption across a wide concentration range, cells with and without EPS showed the same sorption capacity towards Pu(IV). Oxidation state analysis of Pu in the supernatant indicates near complete reduction of Pu(V) in the presence of cells containing bound-EPS, but not with EPS-free cells, suggesting that bound-EPS promotes Pu(V) reduction. Bound-EPS extracted from *Pseudomonas* sp. also promoted rapid reduction of Pu(V). With ^{13}C labeled glucose as the carbon source, we extracted ^{13}C enriched bound-EPS and examined its composition using Nuclear Magnetic Resonance spectroscopy (NMR). The bound-EPS is primarily comprised of polysaccharides, a number of low molecular weight compounds, and aromatic functional groups, phosphorous functional groups were identified. The potential roles of these functional groups in Pu complexation and reduction will be discussed. Prepared by LLNL under Contract DE-AC52-07NA27344.

Redox Dynamics of Hg and U: Mn(II) as a Reductant of Hg(II) and the Influence of Mineral Surface Sites on the Speciation of U(IV)

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Uranium (U) and mercury (Hg) are contaminants of concern at DOE sites such as Hanford, Rifle, and Oak Ridge. Reductive remediation has been explored extensively for U immobilization, under the premise that mobile U(VI) transforms to less-soluble U(IV) species. As reductive approaches are implemented it is important to understand the effects on other contaminants and components in the system. One of the aims of the Argonne Subsurface SFA project is to provide new insight on the relationship between contaminants of interest (Hg and U), bacteria, and major redox-active elements such as Fe, S, and Mn.

As part of these efforts we have investigated the reduction of Hg(II) by Mn(II). The abiotic reduction of Hg(II) occurs in addition to microbial reduction and is a key component of Hg biogeochemical cycling. Although reduction to Hg(0) is thermodynamically favorable when coupled to the oxidation of Mn(II), to date the redox reactivity between Hg(II) and Mn(II) has not been documented. Here, we use synchrotron X-ray Absorption Spectroscopy (XANES and EXAFS) to demonstrate that Mn(II) can reduce Hg(II) under environmentally relevant conditions. The reactivity, the reaction pathways, and the reduced Hg products depend on pH and the complexing ligands or the mineral loading in the system. At pH 7.5 Hg(II) was reduced to Hg(0) within hours. Hg(II) reduction was coupled to the oxidation of Mn(II) to sparingly-soluble Mn(IV) oxides. Minerals such as Al₂O₃ and TiO₂ inhibited the rate of Hg(II) reduction. Complexing ions such as sulfate-stabilized Hg(I) intermediates, which transformed to Hg(0) over an extended period of time.

In addition, we are continuing to investigate the factors responsible for the non-uraninite U(IV) speciation observed in reduced field-site sediments. We have shown previously that phosphate and Ti(IV) inhibit uraninite formation, resulting instead in complexed U(IV) in the solid phase. Here, we demonstrate that the ratio of U to the high affinity surface sites in a system affects the speciation of U(IV) produced by reduction of U(VI). At low U:surface ratios that are typical of natural environments, the presence of minerals such as TiO₂ and Fe₃O₄ leads to the stabilization of adsorbed U(IV) species, whereas higher U:surface ratios that are more typical of laboratory experiments lead to the predominance of uraninite. These results expand the set of biological and abiotic factors known to control non-uraninite U(IV) speciation and suggest the need to modify current geochemical models to include this complexity for more accurate predictions of U transport.

Diel mercury-concentration variations in a mercury impacted stream

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Diel concentrations of filtered and particulate mercury (Hg) and methylmercury (MeHg), and associated water quality parameters, in East Fork Poplar Creek (Tennessee, USA) were evaluated bi-hourly for a 30-hr period during the summer and winter seasons to determine if biogeochemical Hg and MeHg cycles respond to the daily photocycle. This creek is contaminated with high levels of inorganic Hg (baseflow unfiltered Hg ~70 ng/L). Results from the summer field campaign revealed a doubling of particulate Hg and MeHg concentrations during the nighttime periods concurrent with increases in total suspended sediment; diel changes in the activity of macrobiota affecting the suspension of contaminated sediments is likely responsible for these patterns. There were no diel patterns in filtered Hg (~11 ng/L) or dissolved organic carbon quantity (~2 mg/L) or quality (SUVA-254 ~2.7 L/mg C/ m). Dissolved gaseous Hg (Hg(0)) concentrations, measured on a subset of samples, peaked mid-day (0.45 ng/L) with a minimum measured just prior to sunrise (0.20 ng/L) likely reflecting the effects of Hg photo-reduction; overall, Hg(0) represents a small fraction (<1%) of Hg in the system therefore a diel cycle is not observed in the bulk Hg measurement. Concentrations of filtered MeHg varied, with daytime increases of ~50% over nighttime concentrations (nighttime low of 0.22 to a mid-day maximum of 0.31 ng/L) representing about one third of the variability observed for a morning sample over the annual cycle (from 0.1 to 0.4 ng/L). Elevated daytime concentrations relative to nighttime indicate that photo-demethylation is not a dominant process in this stream in the summer, possibly due to shading from overhanging vegetation during the growing season. The large variability in dissolved MeHg, which appears to be correlated with the daily photocycle, implies key controls on net methylation occur within the stream or on the stream bed. Reasons for daytime highs include factors such as small scale temperature increases in the water column and photosynthetic activity of stream biofilm generating conditions that promote methylation. Periphyton biofilms in wetlands and lakes and epiphytic microbial communities on a dominant filamentous alga in one stream system have been implicated in methylmercury production; however, further research is required to determine the role of in-stream biofilms to MeHg patterns in this stream system.

PNNL SBR SFA: Data Management and Assimilation

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Management and assimilation (DMA) of diverse data sets generated from multi-scale observations, field experiments, and modeling is an integral part of the PNNL SBR SFA that cuts across all tasks. It is an essential activity to bridge multi-scale field and process model studies, and multi-scale science and modeling as proposed in PNNL's new SBR SFA Science Plan. Making data and modeling results from our SFA research available to the broader scientific community and the public is critical to advancing DOE's mission. Our DMA goals are to establish and maintain a central repository for storage and dissemination of project data sets and to improve model predictability through iteration between model conceptualization and experimental/field data. The expected products of DMA are (1) a comprehensive database that includes laboratory and field data and modeling results with linkages to the DOE PHOENIX database, BER/BSSD KBase, and the EMSL data management system and (2) a community data assimilation framework employing high performance computing and adapted for multi-scale science and modeling.

This poster illustrates representative data products generated by PNNL SBR SFA research team over the past triennial period, highlighting the use of telemetry for robust real-time data collection. This poster also demonstrates how multi-scale and multi-type data are assimilated using a Bayesian framework to characterize scale-dependent heterogeneity and reduce uncertainty in model predictions.

Iron and organic matter dynamics under fluctuating redox conditions

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The co-precipitation of Fe and organic matter (OM) is common in soils, sediments, surface water and subsurface aquifers, systems that experience significant variation in either redox, or pH conditions. The abundance of Fe in almost all natural soils and sediments combined with the enormous quantity of carbon stored in soils means that Fe-OM interactions likely have a quantitatively significant impact on global carbon cycling. It is suggested that the association of OM with Fe oxyhydroxides hinders its biodegradation, but the mechanism behind these reactions is not entirely understood, and may depend on the type of OM (e.g. polysaccharide-, protein-rich, etc.) and Fe oxyhydroxide, on the type of functional groups involved in Fe complexation (e.g. carboxyl), or on the means of association, (e.g., OM adsorption, formation of OM-mineral co-precipitates, OM occlusion). The goal of this work is to improve our understanding of organic matter-Fe oxyhydroxide interaction in natural settings, and propose a mechanistic example of C and Fe dynamics under fluctuating redox conditions. A series of naturally occurring ferrihydrite samples that underwent in situ reductive transformation in groundwater at the Rifle, Colorado field site were characterized in parallel with model compound/Fe(III) co-precipitates (alginate, albumin, amylose) in order to (1) examine C spectroscopic signatures that indicate Fe-OM complexation, and (2) determine OM types and their spatial distribution in relation to Fe. The mineralogy, composition, and Fe and C speciation were characterized using several synchrotron-based diffraction, nm-scale imaging and spectroscopic techniques. Results obtained for synthetic model compounds allowed us to attribute C NEXAFS spectral shifts to Fe complexation, and these were used for the interpretation of C NEXAFS obtained for the natural samples. The mineral-associated OM fraction in the natural samples exhibits variable C spectroscopic signatures as reductive transformation reactions progressed. Additional OM heterogeneity was observed in the most reduced samples in terms of OM type and association with Fe(II)/(III) phases. Possible reaction pathways between C and Fe will be discussed based on these results.

Isotopic Evidence for Biogeochemical Interactions Between the Unsaturated Zone and Groundwater in the Rifle Floodplain

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One of the primary goals of the LBNL SFA 2.0 is to gain an understanding of the impact of microbial activity on the mobility of carbon in unsaturated environments. Our initial study site is the Old Rifle floodplain in western Colorado. The unsaturated zone at the site consists of alluvial sediments covered by approximately 2 m of locally sourced clean fill material overlying a 3-4 m thick perched aquifer. As part of SFA 2.0, depth-distributed gas samplers and suction lysimeters for pore water sampling were installed through the unsaturated zone at three different locations across the site. The concentrations and isotopic compositions of water and soil gas components have been monitored over the past year in order to gain insights into microbial activity in the unsaturated zone.

A combination of water isotopes and the isotopic composition of porewater strontium and uranium has been used to track infiltration of water through the unsaturated zone. Seasonal variations in the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of precipitation are smoothed out in the upper part of the unsaturated zone and the average values are essentially the same as the groundwater making it impossible to use natural water isotopes to distinguish infiltration through the vadose zone from regional groundwater flow. To address this, we conducted an artificial snow event using deuterium-labeled snow in late February. Shifts in pore water $\delta^2\text{H}$ values have been observed 2 m below ground surface, suggesting relatively rapid infiltration pathways for some surface waters. Vadose zone porewater is characterized by high $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr concentrations. The influence of this strontium on the groundwater suggests that as much as 20% of the groundwater strontium is derived from vertical recharge.

Insights into metabolic activity in the unsaturated zone have also been gained from isotopic measurements. The $\delta^{13}\text{C}$ of CO_2 in the soil gas is in isotopic equilibrium with groundwater DIC and not bulk organic carbon in the vadose zone soils or dissolved organic matter in the pore water. This implies that high CO_2 concentrations (to >5% during the summer) in the lower part of the unsaturated zone are largely due to exchange of inorganic carbon between the groundwater and the pore gases and not heterotrophic microbial metabolism. Isotopic signatures of other vadose zone components, including the $\delta^{15}\text{N}$ of N_2O and the $\delta^{34}\text{S}$ of porewater sulfate indicate that denitrification and sulfate oxidation may be important processes during certain times of the year.

Organismal and Environmental Level Investigations of the Mercury Methylating Genes *hgcAB*

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The discovery and verification of the mercury methylation genes, *hgcAB*, has been a seminal discovery by the ORNL Hg SFA. Their discovery now opens up new avenues of research. A consequence of this discovery is verification of the prediction that the *hgcAB* genes can be used as a prediction of a cell's capability to methylate mercury. Validation of this prediction has allowed for Hg-methylating organisms to now be identified in both the bacterial as well as archaeal branches of the tree of life and this activity now encompasses all anaerobic metabolisms from primary fermentors through to the methanogens. The latter is particularly relevant to agricultural environments as well as treatments plants. A recent question that has come to light as a result of this work is why are the rates and extents of methylation vastly different in methylating organisms when the same genes/proteins are involved, and we are working to address this question.

A scanning of all metagenomes to date reveals that while the *hgcAB* gene pair is relatively rare, there are environments where the genes appear to be more abundant than others. These more abundant environments include a variety of sediments and polluted marine areas as well as northern latitude permafrost while being almost absent from mammalian microbiomes and marine/ocean environments. However, differences in sequencing technologies, depth of coverage and other factors make direct comparisons difficult at best. From the apparently more abundant environments, identification of the organisms possessing the gene pair was overall successful except that there were no known organisms to correlate the *hgcAB* gene sequences to for the oxygen minimum zone of the North Pacific Ocean, permafrost in Bonanza Creek, AK or the hypersaline soda lakes. Further, several cases were found where these two genes appeared to be fused in *Pyrococcus furiosus* and uncultured members of the OP8 and OP9 candidate divisions. *P. furiosus* was not able to methylate Hg, suggesting that the gene fusion eliminated this activity. Further, our analyses suggest that the gene pair may have originated in the Archaea and calls into question whether the two separate genes or the fused genes are the ancestral form. Finally, co-occurrence analysis within the metagenomes suggests that particular pairings of organisms may be preferred and may have facilitated lateral gene transfer of *hgcAB* over time.

Molecular Biology Level Investigations of the Mercury Methylating Genes *hgcAB*

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The discovery and verification of the mercury methylation genes, *hgcAB*, has been a seminal discovery by the ORNL Hg SFA. Their discovery now opens up new avenues of research. Efforts are now underway to determine the mechanism of action that allows for the biotransformation of Hg(II) to MeHg and to be able to detect and quantify the gene abundance and expression in the environment. To these ends, we have determined that replacement of cysteine residues in *hgcA* or *hgcB* that were predicted to be essential for activity are in fact required. These include the cysteines in the active site of *hgcA* as well as those now determined to be required for correct folding of the functional protein. Further, at least one of the two exposed S residues at the C-terminal end of *hgcB* are required for Hg-methylation to occur. In an effort to understand the mechanism of action and to determine the stoichiometry of *hgcA* to *hgcB* as well as to determine the plausible requirement of other protein(s), we are developing genetically tagged strains and antibodies for purification of the functional complex.

Detection of these genes in the environment is essential to understanding the relationships between geochemical parameters and the biological generation of MeHg. To this end, we have developed degenerate primers for the qualitative and quantitative assessment of *hgcAB* at the genetic and transcriptomic level for each of the Deltaproteobacteria, Firmicutes and Archaea. The primers have been optimized and tested against a variety of pure cultures of known methylators and known non-methylators as well as against a variety of environmental samples. Currently, we are correlating these molecular biology level results with the assessed geochemical and physicochemical parameters for each environment.

Identification and quantification of mercury binding functional groups in natural organic matter and methylating bacteria

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Our recent studies have emphasized the important role of thiols in controlling the fate of mercury (Hg) species, including highly toxic methylmercury, in both biotic and abiotic systems. Reactions of inorganic Hg species with naturally dissolved organic matter (DOM) results in both reduction of Hg(II) and oxidation of Hg(0), suggesting the involvement of two competing mechanisms: reduction by reduced semiquinones and oxidation by thiol-induced complexation. Similar effects of cellular thiols on Hg reduction, oxidation, and cell-surface binding have been observed on mercury-methylating bacteria, such as *Geobacter sulfurreducens* PCA and *Desulfovibrio desulfuricans* ND132. However, a robust and sensitive measurement approach for identifying and quantifying thiols present in complex DOM and bacteria remains an analytical challenge due to low abundance of thiols, their susceptibility to chemical oxidation, and the inherent absence of distinguishing spectroscopic characteristics. In this study, we describe the development of a thiol-specific fluorescent labeling technique to quantify thiols on bacteria and DOM in environmental samples. We report successful detection and quantification of nanomolar concentrations of thiols in washed cells of Gram-negative bacteria directly in phosphate buffered saline and DOM in aqueous solution. We further explore the use of high-throughput analytical approaches such as high-resolution mass spectrometry to profile molecular compositions of DOM and to describe the interrelated transformations of compounds in DOM following its exposure to Hg. We discuss the identification of the key molecular species that participate in Hg complexation and redox reactions with important implications to the bioavailability and microbial methylation of Hg in the environment. The diversity (or lack thereof) of reactive thiols requires additional study as this information could be useful in predicting the impact of Hg-cell binding or Hg-DOM complexation, Hg uptake by methylating bacteria, and Hg transformation in the environment.

System Fluxes: Task 1

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Task 1 of the FY15-17 PNNL SBR SFA Plan will assess the effects of daily, seasonal, and yearly variations in the hydrologic cycle and climate on groundwater-surface water interactions, contaminant mobilization and transport, and C and N concentrations/emissions from the SIZ at the reach scale and their feedbacks to climate. The task aims to improve reach-scale understanding of the spatial and temporal dynamics of biogeochemical cycling in the SIZ, their interactions with the water cycle, and feedbacks to climate through observational studies, data synthesis, and integration of Task 2 and 3 results into reach-scale models, and to develop a facies-based classification of SIZ environments along a river reach through synthesis of existing data and new measurements, and to establish a methodology with Tasks 2 and 4 to use these for reach-scale predictions of SIZ controls on contaminant, C, and N fluxes.

To achieve these goals, reach-scale data and results from other tasks will be assembled and integrated into a community-modeling framework to advance understanding of SIZ processes and their contributions to reach-scale hydrochemistry. The new model framework to be established include three modeling components extending from upstream (i.e., Priest Rapids Dam) to downstream (Richland, WA) boundaries of the Hanford Reach. These components will be developed in a parallel but integrated fashion as follows: i) a facies model of the SIZ; ii) a terrestrial component from canopy top to the SIZ bottom that incorporates SIZ processes; and iii) a riverine component to simulate in-stream processes and their linkages to the SIZ. Centered on the facies concept, the terrestrial and riverine components will be coupled to represent interactions between the river and groundwater through advection, dispersion, and diffusion. By applying the modeling framework at the reach scale and beyond, we seek fundamental insights on the impacts of dynamic water exchange between the SIZ and the river on critical reach-scale microbial and ecological functions that regulate riverine C and N budgets, and on the potential influences of climate change (e.g., increased stream temperature and oscillation of river stages) on the highly coupled riverine-SIZ environment, and in turn, biogeochemical fate and transport processes and their feedbacks to regional climate.

The LBNL Sustainable Systems Subsurface Biogeochemistry SFA 2.0: Overview

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The LBNL Sustainable Systems SFA 2.0 is advancing approaches for quantifying and simulating genome-through-watershed scale interactions that govern biogeochemical cycling in terrestrial environments. The terrestrial environment is an especially complex component of the Earth System: it is the host for a multitude of interactions among plants, animals, microorganisms, minerals, migrating fluids, and dissolved constituents that occur within a heterogeneous framework and across a wide range of scales. There are significant uncertainties associated with the predictive understanding of terrestrial environment biogeochemical cycling relevant to carbon cycling, contaminant mobility and biofuel crop sustainability.

The SFA 2.0 is developing approaches to quantify how climate or land-use-induced changes in hydrology and vegetation affect subsurface carbon inputs, spatial and temporal distribution of flow and transport, biogeochemical cycling, and microbial metabolic activity in terrestrial environments; how will these processes change over time; and what effect these interactions have on overall watershed biogeochemical functioning. These questions are being addressed through iterative and multi-scale experiments and observations tied to the development of a Genome-Enabled Watershed Simulation Capability (GEWaSC). GEWaSC will provide a community predictive framework for exploring how genomic information stored in a subsurface microbiome affects biogeochemical watershed functioning, how watershed-scale processes affect microbial functioning, and how these interactions co-evolve.

Development of approaches and initial investigations are being carried out at the Rifle, CO subsurface biogeochemistry community field study site, which is located in a Colorado River floodplain. At this site, seasonal snowmelt and perturbation experiments are being used to explore how hydrological changes in moisture and dissolved oxygen affect subsurface carbon transport, biogeochemical transformations, and metabolic potential across the floodplain, as well as to test developing GEWaSC capabilities for predicting metabolic and geochemical in the presence of vertical and lateral heterogeneity.

Launched in October of 2013, the LBNL SFA 2.0 project has already made substantial progress along several critical and linked research fronts. Examples include: metagenomic analysis revealing the extraordinary genomic diversity of aquifer microbiomes and their roles in terrestrial system biogeochemical cycling; new soil, vadose zone and groundwater biogeochemical instrumentation and monitoring that has revealed high spatiotemporal variability of DOC in response to hydrological pulses; new approaches for quantifying organic-mineral associations; new approaches for remotely identifying hotspots of microbial activity in the Rifle floodplain, field manipulation experiments to probe metabolic and geochemical responses; and progress in developing a genome-enabled watershed simulation capability.

The Molecular Basis of Mercury Methylation: Expression, Purification and Characterization of HgcA

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Mercury (Hg) is a pervasive global pollutant which, as methylmercury (MeHg), bioaccumulates in the food web and is highly toxic to humans and other organisms. Unlike inorganic forms of mercury, which originate from atmospheric deposition and point discharges, MeHg is generated in the environment predominantly by anaerobic microorganisms. The biosynthesis of methylmercury has been associated with *hgcA* and *hgcB*, two genes unique to methylating bacteria in anaerobic environments. Homologs of these two genes have been identified in 72 bacterial species with sequenced genomes. The genes encode a corrinoid protein, HgcA, and a 2[4Fe-4S] ferredoxin, HgcB, consistent with roles as methyl carrier and electron donor required for corrinoid cofactor reduction, respectively. However, the specific role of HgcA and HgcB in the context of carbon and energy metabolism of anaerobic bacteria remains unclear. Homology modeling suggests an unprecedented coordination of a cysteine thiolate to the Co center of the corrinoid cofactor of HgcA.

The HgcA cobalamin binding domain (CBD) was obtained by heterologous expression in *E. coli* using four separate fusion tags to identify a construct with enhanced solubility. After purification by ion exchange chromatography and gel filtration under strictly anaerobic conditions, the HgcA-CBD was reconstituted with its cobalamin cofactor *in vitro*. The reconstituted protein is subject to biophysical characterization, including UV-Vis, CD, EXAFS and EPR, to investigate its overall structure, identify axial Co coordination ligands and redox chemistry. Recently, we have obtained first samples of isotopically labeled (¹³C, ¹⁵N) HgcA-CBD for structure determination by NMR spectroscopy at EMSL. In concert with computational studies, the biophysical, functional and structural characterization of HgcA will advance our understanding of the molecular mechanisms leading to the biosynthesis of toxic MeHg by methylating bacteria.

Synchrotron-based characterization of the physical and chemical characteristics of carbon in the subsurface and root zones to improve Earth system modeling of biogeochemical cycling of carbon

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Mechanistic understanding of carbon (C) biogeochemical cycling is essential for the development of Earth System Models. Critical for that mechanistic understanding is determination of physical characteristics and chemical speciation of C in subsurface and root zone environments. Hard x-ray microtomographic imaging of soil pore structure in soil aggregates is a powerful approach to understanding physical structure and controls of C partitioning within soils. X-ray spectroscopy- and microscopy-based investigations of constituents of subsurface and root zone materials can provide critical insights into the chemical nature of C in these materials. Although soft x-ray scanning transmission x-ray microscopy (STXM) can provide spatially resolved chemical information about C in samples, the thickness and hydration state of environmental samples often preclude the utility of soft x-rays. This limitation can be overcome with the x-ray Raman technique, which enables measurement of C 1s x-ray absorption (XAS) spectra using high energy x-rays. We are integrating x-ray microtomographic, Raman, and STXM approaches to develop a mechanistic understanding of C cycling.

We are investigating the feasibility of locating a soft x-ray STXM beam line as a "side branch" on an APS bending magnet beam line already developed for XAS. Use of x-ray optic components recycled from decommissioned beam lines will drastically reduce the cost of developing such a capability. Integrating these approaches into our research will provide spatial resolution information that will be complementary to x-ray Raman measurements of bulk samples.

Our x-ray Raman investigations of C speciation in a variety of standards, microbial biomass, and soil constituents from peats, humic materials, Alaskan permafrost and Spruce Site soils showed that x-ray Raman measurements can distinguish important C moieties like aromatic-C, amide-C, phenol-C, carbonyl-C, and carboxyl-C. Comparisons of results with nuclear magnetic resonance measurements indicate agreement and complementarity of the two approaches.

We have also investigated the pore space and physical structure of three size classes of soil aggregates (250-425, 425-841, and 841-100 μm) collected from a grassland field to determine correlations between aggregate size, internal pore structure, and microbial community composition within aggregates. X-ray transmission microtomographic measurements indicated a greater proportion of the pore space in the small- and medium-sized macroaggregates is present as relatively smaller pores, resulting in greater overall porosity and pore-mineral interface area. Building on this approach, we have also begun technique development with the ultimate goal of imaging the spatial arrangement of microorganisms and metabolic processes within opaque media such as soil aggregates.

Identifying Molecular Scale Mechanisms Controlling Actinide Transport

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The Subsurface Biogeochemical Research Scientific Focus Area at Lawrence Livermore National Laboratory is focused on identifying and quantifying the biogeochemical processes that control the fate and transport of Pu and other actinides at environmentally relevant concentrations ($1\text{E}-12$ - $1\text{E}-18$ mol/L). We are taking advantage of LLNL's unique capabilities in (1) measuring actinide concentrations at ultralow concentrations ($<1\text{E}-14$ mol/L) by AMS (2) characterizing the morphology of Pu associated with mineral surfaces and microbes by TEM and SEM, and (3) investigating the structure and reaction kinetics of actinide complexes by NMR. Additional capabilities at Clemson University (e.g. FTIR) are employed to elucidate the nature of ternary actinide-organic-mineral complexes.

Recent flow cell sorption/desorption experiments have been used to quantify reaction kinetics. Both equilibrium isotherm data and desorption kinetic data indicate that Pu sorption behavior at environmentally relevant trace concentrations ($1\text{E}-15$ M) is equivalent to observations at higher concentrations ($1\text{E}-10$ M). Rate data are being used to assess the stability and migration potential of Pu under environmentally relevant timescales and distances.

Unique longterm (~ 3 year) nuclear melt glass alteration experiments are examining secondary mineral formation (including colloids) across a range of temperature (25 - 200 °C) and the association of Pu with colloids. Follow-on experiments are investigating the nature of these Pu associations (e.g. coprecipitation, sorption).

The stability of Pu on colloids and mineral surfaces is dependent on its redox state. Recent studies examined the role of trace peroxide in surface water and groundwater on the mobilization of Pu. Fenton reactions lead to oxidation (and mobilization) of Pu. However, these reactions are pH dependent, transient, and their effectiveness is dependent on the nature of mineral surface to which Pu is sorbed.

NMR has proved to be a unique tool for exploring reaction kinetics (and surface structure) of actinide complexes. Recent investigation of the Np(VI) tris-carbonato complex has identified proton-enhanced and proton-unenhanced ligand exchange pathways that parallel those of U(VI). These experiments are revealing previously unknown patterns in reaction kinetics among the actinides.

Ternary sorption studies (actinide-NOM-mineral) have been performed to examine the role of organic matter in actinide transport. Column studies using radiolabeled NOM and hematite colloids in the presence of either Th(IV) or Pu(IV) have shown that NOM coatings on colloid surfaces can prevent aggregation and enhance transport of colloid bound Pu/Th. Specific binding of the NOM to mineral surfaces has been characterized using ATR-FTIR spectroscopy.

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LBNL Sustainable Systems SFA 2.0: Genome-enabled watershed simulation capability (GEWaSC)

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The LBNL Sustainable Systems 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 initial development stages of a Genome-Enabled Watershed Simulation Capability (GEWaSC), which will provide a predictive framework for understanding how genomic information stored in a subsurface microbiome affects biogeochemical watershed functioning, how watershed-scale processes affect microbial function, and how these interactions co-evolve. This multiscale framework builds on a hierarchical approach to multiscale modeling, which considers coupling between defined microscale and macroscale components of a system (e.g., a catchment being defined as macroscale and biogeofacies as microscale). The multiscale framework is based on an object-oriented, modular software design that couples individual process models (e.g., biogeochemistry, microbial function). Initially, we are focusing on biogeochemistry within the Rifle floodplain system, a component of the greater Colorado River system. At the floodplain scale, our model schema considers microbial competition and activity in discrete zones (biogeofacies) identified using a combination of biological, chemical, and geophysical approaches. These zones include surface soils with vegetation, the vadose zone and capillary fringe, and naturally reduced zones with buried organic material.

We also report our initial progress in the development of a trait-based modeling approach within a reactive transport framework that simulates coupled guilds of microbes. Guild selection is driven by traits extracted from, and physiological properties inferred 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 unequivocal. 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 chemolitho(auto)trophs. Metabolism of exogenous substrates fuels 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 initial simulations to identify the processes regulating aquifer oxygen concentrations during seasonally fluctuating water table regimes at the Rifle floodplain.

Microbial cell surface interactions and biogeochemical controls on mercury (Hg) redox transformation and methylation

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Methylmercury (MeHg) is produced primarily by certain anaerobic bacteria, such as *G. sulfurreducens* PCA and has received extensive interest due to its trophic transfer and bioaccumulation in biota. Although the genetic basis of bacterial methylation of mercury (Hg) is recently discovered, the biogeochemical processes controlling of Hg bioavailability and uptake are not fully understood. We previously showed that PCA cells can reduce, adsorb, and methylate mercuric species, Hg(II), but it remains unclear how the reduction and adsorption processes affect Hg methylation and whether this organism can also oxidize dissolved elemental Hg(0), thus affecting Hg speciation and methylation through redox transformations. Here, we employ kinetic experiments to gain insight into how microbes affect Hg redox transformation and whether cell-Hg association may influence Hg uptake and methylation. We show that PCA cells are capable of not only reducing Hg(II) but also oxidizing dissolved elemental Hg(0) under anaerobic conditions. The kinetics of this transformation is determined by the cell biomass (or cell thiols) to Hg ratio. We further examined the correlations between Hg-cell interactions (e.g., adsorption, reduction and oxidation) and methylation at given cell to Hg ratios. At a low cell to Hg ratio, Hg(II) reduction was dominant; whereas at a high cell to Hg ratio, oxidation of Hg(0) to Hg(II) became a dominant process. Mercury methylation was positively correlated to cell adsorption ($r = 0.96$) but negatively correlated to Hg reduction ($r = -0.87$). The inverse correlation between reduction and methylation was verified using a PCA mutant, $\Delta\text{omcBESTZ}$, which is deficient in five outer membrane c-cytochrome genes but possesses two times higher cell-SH than that of the wild type. Similarly, using the methylation deficient mutant, ΔhgcAB , with a lower abundance of cellular thiols than the wild type, we observe increased Hg reduction but decreased adsorption and intracellular uptake of Hg by the ΔhgcAB cells. Our research highlights the need to consider complex Hg-cell interactions and/or biogeochemical controls on Hg speciation, uptake and methylation in natural environments.

Hydro-Biogeochemical Process Dynamics in the Groundwater-Surface Water Interaction Zone: Fundamental Mechanisms and Mechanism-based Models

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This presentation will describe our research plan on the mechanistic part of the new PNNL SFA research plan: Hydro-Biogeochemical Process Dynamics in the Groundwater-Surface Water Interaction Zone (abbreviated as SIZ hereafter). The research is to fill the knowledge gaps including fundamental biogeochemical processes governing coupled organic carbon, nitrate, and contaminant (Tc and Cr) transformation and gaseous species production (CO_2 , N_2O , and CH_4) in SIZ sediments; key metabolic pathways, enzymes, and functions regulating biogeochemical processes and their applications in constructing biogeochemical reaction network and dynamic models; and subgrid heterogeneity, fine-scale facies and distribution, and their effect on the manifestation and scaling of biogeochemical reaction network and dynamic models. Research will be driven by large, field scale observations and evolving science questions from other elements in the PNNL SFA plan, and will provide: 1) a biogeochemical reaction network and dynamic metabolic models that incorporate key metabolic pathways, enzymes, and functions regulating C, N, and contaminant transformation; and 2) biogeochemical reactive transport models incorporating the effect of subgrid heterogeneity on biogeochemical reaction network and dynamic metabolic models for the applications at large scales.

Flow-through laboratory experiments using the sediment cores from the SIZ will be used for identifying redox active fine-scale facies where organic carbon metabolizes in coupling with the reduction of contaminants (NO_3 , Tc, and Cr) and gaseous species production (CO_2 , N_2O , and CH_4). The redox active materials will then be isolated for mechanistic studies of biogeochemical reactions, functional genes, and key metabolic pathways and enzymes, which will be used for development of biogeochemical reaction network and dynamic metabolic models to describe organic carbon metabolism and contamination transformation. The effect of subgrid heterogeneity and redox active facies distribution on the manifestation and scaling of biogeochemical reaction network and dynamic metabolic model will be rigorously evaluated in reactive transport systems. The derived knowledge and biogeochemical models will be used for large scale applications in other elements of the SFA.

This presentation is part of SBR/PNNL_SFA

Characteristics of the Hanford Reach of the Columbia River Groundwater-Surface Water Interaction Zone for Investigating Hydro-Biogeochemical Process Dynamics

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The Pacific Northwest National Laboratory SBR Science Focus Area is conducting fundamental research on hydro-biogeochemical process dynamics in the subsurface interaction zone (SIZ), where groundwater and surface water mix. The initial site of investigation is a 65-kilometer section of the Hanford Reach of the Columbia River, adjacent to the U.S. DOE Hanford Site. The proposed study site has several characteristics making it an excellent choice for study. There is variable permeability in the riverbed and the adjacent aquifer, with complex heterogeneity throughout the study area. The width and thickness of the SIZ is highly dynamic, due to the heterogeneity of the riverbed and the aquifer, and complex variations in river discharge that occur on multiple time scales, a key feature for addressing SFA research objectives. Complex variations in river discharge, caused by seasonal variations and flow regulation at upstream dams, drive large incursions of river water into the alluvial aquifer system and result in a SIZ that can extend in excess of 250 m from the river bank. Preliminary studies indicate profound changes in contaminant biogeochemistry, microbial community structure, and fluxes of C and N due to mixing of groundwater and river water in this dynamic SIZ. Several contaminant plumes currently discharge into the study site, including uranium, Cr(VI), ⁹⁰Sr, NO₃, and 3H₂O, with ¹²⁹I and ⁹⁹Tc plumes expected in the future. World class data and infrastructure are already in place, including > 500 aquifer tubes and > 250 nearshore wells with interpreted hydrogeology and well data. By taking advantage of the significant level of characterization already completed on the Hanford Site and adjacent Reach, high-impact research can be conducted on SIZ processes with no delay. Science questions addressed, multi-scale approaches, and models developed at the proposed study site would be relevant to a large class of glaciofluvial alluvial aquifers that are common in North America, Europe and Asia. These gravel-dominated systems tend to have high permeability and pronounced heterogeneity. While the alluvial aquifer in the Hanford Reach has high permeability and a wide SIZ, it is well within the range of properties displayed by other glaciofluvial aquifer systems. As a snowmelt-dominated river, the impact of climate change on the timing, magnitude, and temperature of river water intrusions into the Hanford Reach is a significant unknown, and the results of proposed studies on the potential impacts of climate change on SIZ processes would be relevant for many glaciofluvial aquifers.

Hydro-Biogeochemical Process Dynamics in the Groundwater-Surface Water Interaction Zone: Macroscopic Processes

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The subsurface zone into which surface water (e.g. river water) intrudes and mixes with groundwater (SIZ) is a major pathway for chemical transfer between terrestrial and aquatic systems. It is a more biogeochemically reactive domain than either groundwater or surface water because within the SIZ, superposition of limiting nutrients from different sources, including O₂, C, and N, stimulates biological activity. It is a unique domain where microbial processes link biogeochemical transformation and sequestration of groundwater contaminants to mineralization of C and transformation of N from both groundwater and riverine sources. The Hanford Site 300 Area along the banks of the Columbia River is an excellent system in which to study these dynamics because of the detailed understanding of the hydrology and biogeochemistry of the aquifer.

A local (0.1-km²) section of the hyporheic corridor that represents a constrained transect from inland groundwater through the SIZ to discharge points in surface water will be monitored for microbial community structure, biogeochemical activity and hydrology during short- and long-duration surface water intrusion events. Novel ecological modeling techniques will be used to determine relationships between hydraulic conductivity of sediment deposits, biogeochemistry, contaminant transfer mechanisms and rates, and ecological processes shaping microbial communities.

Preliminary data indicates that organic carbon introduced to the SIZ from intruding river water stimulates microbial activity and, through a coupling with denitrification, yields inorganic carbon species. We hypothesize that within low hydraulic conductivity facies, this activity can result in anoxic conditions conducive to immobilization of U. Microbial communities will be analyzed in terms of operational taxonomic unit (OTU) composition via 16S rRNA gene sequencing (iTag analysis) and metabolic potential via shotgun metagenomic sequencing. Abundance of genes involved in C and N cycling and contaminant transport will be monitored and network analysis performed to assess relationships between environmental parameters, measured activity rates and microbial community composition functional potential.

The information generated by this project will be used to generate a predictive local-scale model of contaminant and C-cycling dynamics that will be generalizable to other groundwater-river water exchange systems.

Organic-Mineral Dynamics Component of LBNL SFA2.0

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The Organic-Mineral Dynamics component of the LBL-SFA2.0 has the long term goal of developing an improved conceptual model for OM cycling in the subsurface that can be incorporated into the developing GEWaSC frame work. It takes as its fundamental premise that since the vast majority of organic matter in the subsurface is associated with the solid phase that the processes controlling the up-take and release of OM from the solid phase are key factors in regulating the decomposition of OM in the subsurface. Initial investigations have begun to characterize the chemical form of sediment associated organic matter as a function of subsurface heterogeneity at the Old Rifle, Co. field site. A comparison of Fourier transform infrared (FTIR) spectroscopy data collected on samples provided by the Watershed Controls component shows increased aromatic carbon in high organic matter hotspots across the site, consistent with the observed higher content of particulate plant derived material. FTIR analysis of sediment incubations conducted by the Metabolic Potential component shows a noticeable decrease in aromatic associated functionality after incubations of sediments from those high organic matter hotspots. Furthermore, laboratory OM release experiments using different Rifle materials have been undertaken to determine the buffering behavior of the mineral surfaces on DOM concentration and speciation. Rifle materials placed in organic matter free solutions released OM within hours until DOM concentrations similar to those observed in field samples of 2-3ppm were established. DOM concentration then held constant for a month. The initial composition of the OM as determined by excitation emission spectroscopy was again similar to that observed in pore water extracted from the fresh field materials. Additional analysis of both solid state and extractable OM by FT ICRMS at EMSL is expected to yield further more detailed molecular information. However, these preliminary results emphasize the central role of mineral surfaces in regulating the concentration and structure of DOM. With the assumption that microbial degradation of OM occurs primarily on the DOM phase, this implies a key role for mineral surfaces in controlling OM decomposition across the site.

Geochemical and microbiological response to oxidant introduction into reduced Hanford 300 Area sediments

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Pliocene-age Ringold Formation sediment from below the subsurface redox transition zone (RTZ) at the Hanford 300 Area site was employed in a study of the geochemical response to introduction of oxygen or nitrate in the presence or absence of microbial activity. The fine-grained reduced sediments contained large quantities of reduced Fe in the form of Fe(II)-bearing phyllosilicates, together with smaller quantities of siderite and pyrite. The purpose of the experiments was to assess the potential for native microbial communities to oxidize sediment-associated reduced Fe/S phases in response to oxidant influx, and thereby influence redox balance within the RTZ. A suite of reactors was constructed with dried reduced subsurface material and artificial Hanford groundwater. The reactors were amended with either 10 mM nitrate, anoxic headspace, or no added oxidant. They were inoculated with sediment containing native microbial communities from the either within or below the RTZ. A parallel set of uninoculated sterile controls were also constructed. During a 910-day incubation, a loss of ca. 50% of 0.5 M HCl-extractable Fe(II) (5-10 mmol Fe(II)/L), and detectable generation of sulfate (ca. 0.2 mM, equivalent to 10% of the reduced inorganic sulfur pool) was observed in sterile aerobic reactors. All of the inoculated and the sterile reactors amended with nitrate showed no Fe(II) loss or sulfate generation suspensions despite (1) the recent recovery of chemolithotrophic Fe(II)-oxidizing bacteria from Hanford/Ringold formation sediments, and (2) the detection of genes for CO₂ fixation (Rubisco) in sediments within the RTZ. In contrast, significant nitrate (and, putatively, oxygen) consumption occurred via heterotrophic metabolism took place in the inoculated reactors. In addition, detectable accumulation of Fe(II) and complete consumption of sulfate took place in inoculated oxidant-free reactors. The organic carbon (OC) content of the sediments employed in this study as well as measured OC concentrations within and below the RTZ was sufficient to account for the observed heterotrophic metabolism. Diffusion-reaction simulations of oxygen and nitrate consumption coupled to solid-phase OC oxidation indicate that heterotrophic consumption of oxidants could play a key role in maintaining the redox boundary at its current position. These findings are consistent with a variety of prior observations that Ringold Formation sediments contain active heterotrophic microbial communities, and reveal that such communities are poised to respond to oxidant influx and thereby act as barrier to vertical U, nitrate, and other redox-sensitive contaminant migration over millennial time scales.

Redox Transition Zone Phyllosilicate Reactivity: Thermodynamics and Microscopic Processes

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This research, part of the PNNL SFA, seeks to identify and understand active biogeochemical processes across the redox transition zone (RTZ) of the Hanford 300A site, a regionally expansive subsurface aquitard of fine-grained sediments that displays a dramatic redox transition. These sediments are dominated by Fe-bearing phyllosilicates capable of redox reactions coupled to diffusive biogeochemical fluxes across the RTZ, including C and N. The objective is that through laboratory and simulation of RTZ sediment redox reactivity we can develop a mechanistic understanding of reactions that regulate these climate change gases, as well as contaminant species such as technetium, which can be incorporated into process-based field-scale reactive transport models.

RTZ core samples of oxidized (59-60' depth) and reduced (62-63' depth) material were collected. The clay-sized fraction was isolated from each while preserving native redox conditions and characterized for mineralogy, composition, Fe valence and site occupancy, cation exchange capacity, and redox potential by equilibrating with the AH2DS/AQDS couple. The ferruginous smectite SWa-1 was selected for comparative redox properties characterization and thermodynamic modeling including charge neutralization effects. Molecular simulations were performed using EMSL supercomputing.

Quantitative x-ray diffraction, elemental composition, and cation exchange capacity measurements showed that RTZ oxidized and reduced clay-sized fractions were dominated by Fe-rich montmorillonite (90% and 83%, respectively), a dioctahedral smectite, as the only crystalline Fe-bearing (1.45 and 1.38 mmol/g, respectively) mineral present. The ferrous content was found to be 4.6% and 22.4% of the total Fe, respectively. Synchrotron Fe L-edge x-ray absorption and magnetic circular dichroism spectroscopies showed that the oxidized form is dominated by magnetically ordered octahedral Fe(III) with no apparent tetrahedral Fe(III); an octahedral Fe(II) component is observed in the reduced form. The reduced clay fraction, studied in batch reactors at groundwater pH for Tc(VII) reduction kinetics as a probe of in-ground reduction capacity below the RTZ, in the absence and presence of added aqueous Fe(II), showed that 10% of 10 UM Tc(VII) was reduced in 15 weeks (9 g/L loading) and that this extent doubles after a 58 UM Fe(II) spike. A concomitant loss of octahedral Fe(II) was spectroscopically observed. Molecular simulation shows electron mobility within the octahedral sublattice is 10^5 s⁻¹, consistent with sufficiently rapid electron transfer to adsorbed redox-active species. A thermodynamic model was developed that links Fe-smectite redox properties to biogeochemical parameters such as electrolyte type, concentration, and pH. Plans to incorporate the findings into process-based reactive transport models will be discussed.

Multiscale Science and Modeling: Task 4

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Task 4 of the FY15-17 PNNL SBR SFA Plan will develop an integrative multiscale modeling framework to establish quantitative connections among the suite of models and experiments being developed by Tasks 1-3 across physical and temporal scales. We will develop fundamental understanding of multiscale interactions among scale-specific processes and phenomena, then design the multiscale computational methods and algorithms based on that foundation. We will apply a multiscale modeling framework called the “Multiscale Analysis Platform” (MAP), previously developed by our project team. The MAP embodies a series of questions that guides the user to one of several multiscale modeling motifs, depending on system characteristics. The motifs span a wide range of multiscale modeling approaches from formal upscaling with closure to a number of different hybrid multiscale methods. The MAP approach integrates bottom-up rigorous model development and top-down optimal model deployment into a framework for application-scale modeling in which predictive accuracy and computational burden are balanced. Physics-based model development follows a bottom-up approach that, through rigorous upscaling techniques, allows construction of effective medium (upscaled) representations of fine-scale processes with different degrees of coupling and complexity. A unique element of our approach is the formulation of diagnosis criteria that define applicability ranges of the resulting upscaled representations formulated in terms of macroscale variables. These criteria guide the adaptive top-down use of multiscale hybrid methods where needed (direct linkage to microscale models) together with simpler upscaled models, where applicable, in an optimal (in terms of simplicity and predictive capabilities) deployment of physics-based models for science-informed application-scale predictions. The multiscale framework will employ the Subsurface Interaction Zone (SIZ) multiscale facies concept identified as an integrating element of this research. At each scale of interest, facies will be defined based on available data and the ability to resolve detailed features at that scale. At the fine scale, for example, facies models may differentiate fine-grained domains dominated by diffusive mass transfer (seasonally anoxic) from surrounding advective coarse-textured regions. At the local scale, SIZ facies may reflect stratigraphic structures within the Hanford and Ringold formations that control flow paths of advective groundwater-river water exchange feeding the fine-scale domains. At the reach scale, SIZ facies may reflect the geometry of the Hanford-Ringold interface and paleochannels and their control on bulk river-groundwater exchange rates.

Microbial Extracellular Electron Transfer Mechanism in Hanford Subsurface *Geobacter* spp.

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Iron (Fe) is abundant (i.e., 3.5- 8% by weight) in the subsurface sediments of Hanford 300 area (300A) where Fe(III) and Fe(II) can serve as an oxidant and a reductant for microbial energy generation, respectively. Microbial mediated redox reactions may impact fate and transport of the contaminants, such as Cr, Tc and U, that are commonly found in 300A and other DOE sites. *Geobacter* spp. were identified as the most abundant Fe(III)-reducing bacteria found in the redox transition zone (RTZ) of 300A sediments and the Fe(III)-reducing bacterium *Geobacter* sp. FA1 was isolated from the 300A RTZ. The electron transfer mechanisms for extracellular Fe(III) reduction in these 300A microorganisms are, however, essentially unknown.

Genome analysis of the model Fe(III)-reducing bacterium *G. sulfurreducens* revealed a *Geobacter* porin-cytochrome (Gpc) protein complex that consisted of a porin-like outer membrane protein, a periplasmic c-type cytochrome (c-Cyt), and an outer membrane c-Cyt, which we predicted was responsible for transferring electrons across the outer membrane. The genes that encode the Gpc proteins are adjacent to each other in the genome of *G. sulfurreducens* where the *gpc1* and *gpc2* gene clusters are also co-located. Deletion of both *gpc1* and *gpc2* gene clusters of *G. sulfurreducens* has no impact on growth with fumarate as the terminal electron acceptor, but diminishes the ability of *G. sulfurreducens* to reduce Fe(III)-citrate and ferrihydrite, a poorly crystalline Fe(III) oxide. Complementation with the entire *gpc1* gene cluster restores the ability of *G. sulfurreducens* to reduce Fe(III)-citrate and ferrihydrite. Isolated Gpc protein complexes reconstituted in proteoliposomes are able to transfer electrons across the lipid bilayer from reduced, internalized methyl viologen to external Fe(III). The *gpc* gene clusters are present in all eight sequenced genomes of *Geobacter* spp., the Hanford isolate *Geobacter* sp. FA1 as well as 11 other sequenced bacterial genomes, including the Fe(III)-reducing bacteria *Anaeromyxobacter* spp. and *Desulfuromonas acetoxidans*. Furthermore, the characterized function and organization of the Gpc complex are very similar to that of the Mtr porin-cytochrome extracellular electron transfer protein complexes found in the other Fe(III)-reducing bacteria, such as *Shewanella* spp., and several Fe(II)-oxidizing bacteria, although Gpc and Mtr proteins share no sequence identity. Thus, the porin-cytochrome complex appears to be a common mechanism for transferring electrons across the outer membrane by diverse Fe(III)-reducing and Fe(II)-oxidizing Gram-negative bacteria.

Determining Mechanisms of Hg Methylation by HgcA and intramolecular Hg transfer by MerA at the Atomic Scale

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Our team uses computational approaches to establish the physicochemical underpinnings of mercury (Hg) transformations in the environment in both aerobic and anaerobic contexts. The cobalamin-dependent protein HgcA was recently shown to be required for the production of methylmercury by anaerobic bacteria. In that work, a strictly conserved Cys residue in HgcA was predicted to be a ligand to Co(III), which has never been observed in any protein. Here, our main focus is on determining the detailed mechanism of Hg methylation carried out by HgcA. We have carried out density functional theory (DFT) calculations of model methylcobalamin complexes containing a lower-axial Cys or His ligand to cobalt, the latter of which is commonly found in other cobalamin-dependent proteins. In principle, methylcobalamin can transfer a methyl group as a carbocation, radical, or carbanion, but only the latter two species are plausible for transfer to an electrophilic substrate such as Hg(II). We find that Cys thiolate coordination to Co facilitates both methyl radical and methyl carbanion transfer to Hg(II) substrates, but carbanion transfer is predicted to be more favorable overall when condensed phase solvation effects are taken into account. Our calculations support the proposal that the strictly conserved Cys in HgcA enhances the methylation of Hg(II). In other work, we have investigated the capture and transfer of Hg²⁺ in the principal enzyme involved in bacterial mercury resistance, the mercuric reductase MerA. We performed quantum mechanical/molecular mechanical (QM/MM) calculations to characterize intramolecular Hg²⁺ transfer from the C-terminal pair of cysteines to the active site pair in the catalytic core of MerA. We find that the transport of this soft, divalent cation is made energetically feasible by pairing a competition between multiple cysteine thiolates for Hg²⁺ with a competition between Hg²⁺ and protons for the thiolates. Finally, we have computed the pK_as of the cysteine pair in NmerA, the N-terminal metallochaperone domain of MerA, compared them with experimentally determined values, and here we provide insight into their unique Hg-binding properties.

Water and carbon fluxes into groundwater from a semi-arid floodplain vadose zone

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Water and carbon fluxes from the vadose zone into groundwater need to be quantified to understand subsurface hydrobiogeochemical conditions and predict impacts of climate change. These fluxes are challenging to determine in semi-arid regions because of their low magnitudes. However, the remediated uranium/vanadium mill tailings site on the Rifle, Colorado floodplain possesses characteristics favorable for investigating subsurface transport, including locally derived fill soil with geochemical characteristics typical of the region, an established vegetation cover, geochemically distinct boundaries between the fill and underlying alluvium, predictable groundwater interaction with the adjacent Colorado River, and an impermeable lower boundary (shale at ~7 m depth). Within this well-defined hydrological system, we installed neutron probe access tubes and depth-distributed tensiometers, pore water samplers, and gas samplers along a transect aligned with the groundwater flow direction in order to determine inventories and fluxes of water, carbon, and other components. Seasonally dependent recharge into groundwater is quantified by combining field measurements with laboratory/pedotransfer constraints on hydraulic properties. High dissolved organic carbon (DOC) concentrations in the vadose zone (up to ~10 mM) relative to in groundwater (<1 mM), and increasing CO₂ concentrations with depth indicate the importance of deeper vadose zone OC transport and microbial activity. DOC characteristics and trends are being used to improve understanding of vadose zone fluxes of carbon into groundwater. Variations in carbon availability and water saturations at the capillary fringe are also reflected in changes to redox-dependent chemical components, including residual U and V. This effort is part of Sustainable Systems 2.0, a new Department of Energy project investigating climate-induced changes in subsurface carbon transport, biogeochemical transformations, and metabolic potential of microbial communities.

Sustainable Systems SFA Data Management and Assimilation

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A software platform and infrastructure is being developed for management and assimilation of data collected for the Sustainable Systems SFA 2.0, with components and capabilities based on the SFA 2.0 project priorities. The completed infrastructure will enable integration and synthesis of 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 is to integrate monitoring data and characterization of samples collected at the field site in Rifle, Colorado.

The main elements of the Data Management System that have currently been developed include:

- RifleDB: The Rifle Data Management Web Site (<http://www.rifleifrc.org/>), which is used to host data from the field site. Users with a login to the website can view several datasets, including hydrological data (water levels, water and soil temperatures), geochemical data from groundwater samples, borehole lithological logs, and site meteorological data. The Data Management System also incorporates a data quality process, which is necessary to address user needs and produce quality-checked datasets. The website is implemented as a Zend Framework 2 web application, which sits on top of a MySQL database.

- SFA Google Drive: An internal Google Drive folder that is used for preliminary storage and sharing of data across all SFA components before migrating the data to a database.

- SFA Data Needs Sheet: A Smartsheet that is used to enable tracking of data that are being generated, including data owners and status. Data needs are specified for three domains - the saturated zone, vadose (unsaturated) zone, and general site information. Data items in each of the domains are categorized by a property type - e.g. hydrology, biogeochemistry, microbiology, sediment properties.

Additionally, use case scenarios are being developed to provide input into the development of products that will enable data fusion across the different sources. An example use case highlights integration of depth profile data from the vadose and saturated zones across the TT transect at the Rifle site, including geochemical measurements (concentrations of ions, TIC/TOC, and isotopes in water samples), hydrological measurements and parameters (water level, temperature, soil moisture, hydraulic conductivity and water retention curves), microbiological data (relative abundance of microorganisms and metagenomics), lithological data (borehole logs and particle size distribution), and geophysical data (time-lapse electrical resistivity tomography).

Capturing Transient Climate-Driven Contributions of Surface to Subsurface Processes at Watershed Scales

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The response of humid mid-latitude forests to changes in precipitation, temperature, nutrient cycling, and disturbance is critical to improving our predictive understanding of ecosystem-climate feedbacks to greenhouse gas fluxes and changes in the surface-subsurface energy balance. Predictive understanding of terrestrial systems will require an integrated modeling/experimental approach applied across multiple scales. Recent scientific advances in computing, spectroscopy, and “omics” enable unprecedented process-level studies to address critical knowledge gaps. Mechanistic understanding of the effects of long-term and transient moisture conditions are needed to quantify linkages between changing redox conditions, microbial activity, and soil mineral and nutrient interactions on C cycling and greenhouse gas release in surface to subsurface transition zones. To study these concepts we established transects across hydraulic and topographic gradients in a small watershed with transient moisture conditions. Valley bottoms tend to be more frequently saturated than ridge tops and side slopes which generally are only saturated when shallow storm flow zones are active. Fifty shallow soil cores were collected during timeframes representative of low CO₂ winter conditions and high CO₂ summer conditions. Cores were subdivided into 240 samples based on pedology and analyses of the geochemical (moisture content, metals, pH, Fe species, N, C, CEC, AEC) and microbial (16S rRNA gene amplification with Illumina MiSeq sequencing) characteristics are being conducted. To associate microbial metabolic activity with greenhouse gas emissions we installed 17 soil gas probes, collected gas samples for 16 months and analyzed them for CO₂ and other fixed and greenhouse gasses. Surface water and groundwater data are also available. Parallel to the experimental efforts our data is being used to support hydrobiogeochemical process modeling by coupling CLM with PFLOTRAN to simulate processes and interactions from the molecular to watershed scales. Including above ground processes (biogeophysics, hydrology, and vegetation dynamics), CLM provides mechanistic water, energy, and organic matter inputs to the surface/subsurface models, in which coupled biogeochemical reaction networks are used to improve the representation of below-ground processes. Preliminary results suggest that inclusion of above ground processes from CLM greatly improves the prediction of moisture response and water cycle at the watershed scale. We are investigating the coupled biogeochemical C, N, P, and Fe cycles in the surface and subsurface with improved biogeochemical models that incorporate geochemical and microbial reactions for process-based representation. The results will improve our understanding of the coupled hydrobiogeochemical processes at multiple scales and the representation of these processes in earth system models.

Floodplains as biogeochemical reactors: Using multi-scale approaches to quantify hot spots and hot moments at DOE's Rifle, Colorado field site

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The Lawrence Berkeley National Laboratory's Sustainable Systems Scientific Focus Area (SFA) 2.0 seeks to develop a predictive understanding of how climate-induced changes in hydrology and vegetation affect watershed scale biogeochemical functioning. The "Watershed" component of SFA 2.0 explores the use of multi-scale approaches to characterize terrestrial environments such as floodplain deposits at DOE's Rifle Colorado field site across scales and compartments using geophysical geochemical mineralogical and hydrological datasets. Experiments at Rifle have long focused on stimulated biogeochemical pathways arising from organic carbon injection. Although reductive pathways have been a focus since 2002 ongoing studies are exploring oxidative pathways and their role in mediating fluxes of C N S and aqueous metals. Insights gained from such 'stimulation' experiments are providing insight into analogous natural biogeochemical pathways that mediate elemental cycling in the absence of exogenous carbon. Such reactions are instead mediated by endogenous pools of natural organic matter (NOM) deposited during aggradation of aquifer sediments associated with fluvial processes along the upper Colorado River corridor. Discrete lenses of fine-grained organic-rich sediments (up to 2% organic C and N) enriched in reduced species such as Fe(II) iron sulfides and U(IV) have been identified along the active margin of the floodplain through a combination of geophysical characterization approaches and drilling-recovered aquifer sediments. Referred to as "naturally reduced zones" (NRZs) these localities constitute a distinct facies type (i.e. 'biogeofacies') within an otherwise gravel-dominated largely NOM-deficient matrix. NRZs contain 100-fold higher U concentrations than surrounding aquifer sediments and represent 'hotspots' of seasonally intense C N S and U cycling during excursions in groundwater elevation. Along with recharge by oxic surface waters and groundwater imbibition of air bubbles within the capillary fringe during water level rise is inferred to contribute to seasonally oxic groundwater (both so-called 'hot moment' events) with the impact on redox-mediated reactions exhibiting close correspondence to those induced through intentional introduction of oxidants. Reactions induce sharp gradients in nitrate and sulfate resulting from elevated rates of nitrification and oxidation of reduced sulfur as dissolved oxygen becomes non-limiting. 7-fold increases in aqueous U are observed during this period likely contributing to U plume persistence at the site. Because NRZs contain large stores of NOM and have an outsized capacity to mediate a broad range of redox transformations such 'hotspots' are expected to exert influence over the redox status and biogeochemistry of floodplain deposits worldwide and are thus of broad relevance to subsurface biogeochemists.

Seasonal Hydrology and Biogeochemical Hot Spots: Carbon, Nitrogen and Mineralogic Controls on Suboxic Conditions in the Rifle Floodplain Aquifer

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For most of the year, the Rifle floodplain aquifer is generally suboxic (~0.1 mg/L DO) despite communication with the atmosphere through a ~3 m thick vadose zone. Oxygen can be consumed via heterotrophic microbial reduction as well as the abiotic and microbially-mediated oxidation of reduced species and minerals. While each of these processes are thought to be active, microbial contributions from chemo(litho)autotrophic processes (e.g., ammonia, sulfur and iron oxidation) appear to be prominent.

The snowmelt-driven hydrology of the local catchment and Colorado River results in the seasonal rise and fall of the Rifle floodplain water table. After peaking in June, the initial decline of the water table is associated with elevated DO levels across the floodplain. A notable exception is in the central part of the site near the river, where no significant DO enhancements have been observed. This area is part of a probable naturally reduced zone (NRZ) that has been delineated through spectral induced polarization geophysics, groundwater analyses, chemical and mineralogical characterization of sediment, and biological sampling. The sediments in these NRZs are associated with elevated organic carbon, Fe(II), sulfide, and U(IV).

Coupled variably saturated flow and biogeochemical reactive transport modeling is being used to better understand the interplay of the 1) biotic and abiotic processes maintaining suboxic conditions, 2) the seasonal water table fluctuation and oxygenation, and 3) locally enhanced reactivity in the NRZ. The NRZ is relatively small compared to the floodplain; however, it has a potentially outsized impact on the flow of carbon and nitrogen through the subsurface. Our current GEWaSC focus is on hydrologic and seasonal impacts to the floodplain biogeochemistry in the context of surface and variably saturated flow processes in physically and biogeochemically heterogeneous 3-D sediments. Highly detailed 2-D vertical transect modeling is used to develop and integrate modeling capabilities that fundamentally address the reaction network, stable isotopes, and gas analyses. Highly resolved 3-D modeling extends the conceptual model to the entire floodplain to capture the distribution of lithofacies and NRZs across the site. Large scale 3-D local and regional catchment modeling provides transient recharge to the floodplain due to precipitation, runoff, and evapotranspiration; and inflow and water chemistry from the upland watershed. The omics-informed trait-based reactive transport modeling approach provides a foundation for understanding the impact of hydrologic hot moments and biogeochemical hot spots on the rates of carbon and nitrogen flow through the Rifle floodplain, across spatial and temporal scales.

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

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The PNNL SFA will develop a predictive understanding of the groundwater-surface water interaction zone (subsurface interaction zone, SIZ) and its linkages with the water cycle that 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 critical and ubiquitous domain at the groundwater-surface water interface that regulates contaminant releases to surface waters and associated carbon and nitrogen cycling. Our research plan supports U.S. Department of Energy (DOE) goals to advance a predictive understanding of the biogeochemical structure and function of subsurface environments to enable systems-level environmental prediction and decision support. A key aspect of our plan 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 that enables bi-directional (up- and down-scale) transfer of knowledge, process models, and parameters to the necessary scale of prediction. Using the Hanford Reach of the Columbia River as our 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 will connect SFA biogeochemical transport models across scales while preserving robust process descriptions derived at the local field scale and in the laboratory. New predictive microbial ecological models will be coupled to hydro-biogeochemical models to translate microbial composition into biogeochemical process rates. 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 vulnerable to climate change.

Student Abstracts

Speciation of uranium controls its kinetics of reduction by metal-reducing bacteria

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Uranium bioreduction, the microbial reduction of soluble U(VI) to highly insoluble U(IV), is considered one of the most promising in situ bioremediation strategies to immobilize uranium in the subsurface. The ability to predict the success of uranium bioreduction, however, is complicated by the wide range of geochemical conditions at contaminated sites and the strong influence of uranyl speciation on the bioavailability and toxicity of U(VI) to metal-reducing bacteria. To deconvolute the effects of uranyl speciation on uranium bioreduction kinetics, bioreduction incubations and viability assays with *Shewanella putrefaciens* strain 200 were conducted over a range of pH and DIC, calcium, and magnesium concentrations typically present at uranium-contaminated sites. Results from these incubations were incorporated into a speciation-dependent biogeochemical model able to reproduce the rate of uranium bioreduction across a wide range of geochemical conditions.

The presence of DIC, calcium, and magnesium led to the formation of less bioavailable uranyl carbonate species and decreased rates of uranium bioreduction. The biogeochemical kinetic model described the reduction of uranyl non-carbonate species (e.g. the 'free' uranyl ion, uranyl hydroxide complexes, etc.) with the largest rate constant ($1.2\text{E-}12$ L/cell/day) - orders of magnitude larger than uranyl carbonate ($4.5\text{E-}14$ L/cell/day) and ternary uranyl carbonate species ($8.6\text{E-}21$ L/cell/day) - indicating that non-carbonate species represent the most bioavailable and readily reducible fraction of U(VI) despite being the least abundant species in solution. At high concentrations of bioavailable U(VI), however, bioreduction rates decreased. Viability assays confirmed that the 'free' hydrated uranyl ion is responsible for uranium toxicity to strain 200 and inhibits bioreduction at elevated concentrations. The changes in uranium bioreduction rate across all experimental conditions were successfully predicted by incorporating uranium toxicity into the kinetic model.

Overall, these findings highlight the complex and seemingly counterintuitive influence of uranyl speciation on uranium bioreduction kinetics and identify geochemical conditions that may control uranium bioreduction at contaminated sites. Timely uranium immobilization via bioreduction relies on a delicate balance between maximizing uranium bioavailability and limiting uranium toxicity. These results suggest that efforts to increase uranium bioreduction rates at a given contaminated site by promoting the formation of bioavailable uranyl species will ultimately be constrained by the uranium tolerance of the subsurface microbial community. The new rate law developed in this study may be included in reactive transport models to predict the effect of bioreduction on uranium immobilization over a range of geochemical conditions.

Extensive genomic sampling of subsurface microbes provides a new view of the phylogeny and metabolic potential of the bacterial Candidate Phyla OD1 and OP11

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Our understanding of subsurface microbial communities is limited due to the predominance of members of candidate phyla, which lack cultivated representatives. In particular, members of the bacterial Candidate Phyla OD1 and OP11 are frequently identified in the subsurface. However, the extent of their phylogenetic diversity is largely unknown, and their metabolism inferred only from relatively sparse genomic sampling.

Groundwater microbial communities recovered on 0.2 and 0.1 μm filters from a well at the Rifle Integrated Field Research Challenge site were analyzed prior to and during an acetate amendment. Community genomic DNA was extracted from the filters, sequenced, and assembled. 16S rRNA gene sequences were recovered from assembled data and validated using read mapping-based curation methods. Insertions within 16S rRNA genes were discovered from reference DNA sequence and RNA structural alignments. All 16S rRNA genes were aligned and used to infer a phylogenetic tree. Metagenome scaffolds were binned into genomes based on taxonomic assignment, coverage, nucleotide composition, and time series abundance patterns, allowing for a robust metabolic analysis of uncultivated microbial community members.

Phylogenetic analysis of 1,513 assembled 16S rRNA genes identified ~350 sequence types from members of the OD1, and ~250 sequence types from OP11. On average, these sequences share only 87-88% similarity with reference sequences. Within the complete dataset, 37 bacterial sequences contain large insertions (~500 nucleotides), the majority belonging to the OD1 or OP11 radiations. Most large insertions encode an endonuclease and are predicted to contain either a group I or group II catalytic intron, suggesting that they are self-splicing. Complete genomes for four members of these phyla, along with numerous (250+) genome bins reveal an absence of respiratory pathways, CRISPR/Cas systems, polar flagella, and lipid A synthesis.

Recovery of 16S rRNA genes from groundwater-associated bacteria, and removal of insertion sequences, greatly improves resolution of the OD1 and OP11 phyla, enabling classification at deeper taxonomic levels. The current study greatly expands the phylogenetic distribution of large bacterial 16S rRNA insertion sequences (previously only observed in the Thiotrichaceae). Complete genomes and extensive genome binning confirm the small size of OD1 and OP11 genomes (<1 MB) and their fermentation-based metabolism, whereas enrichment in filtrates suggests small cell size. Future work will overlay the metabolism of additional phyla represented in this complex environment and, combined with time-series analysis, will improve our understanding of the biogeochemical roles of uncultivated subsurface microorganisms.

Organic Matter Sources in the Speciation and Mobilization of Pu in the Subsurface Environment of the Rocky Flats Site

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Plutonium from contaminated soils at the Rocky Flats Environmental Technology Site (RFETS) was found to be concentrated in an organic fraction containing degradation products of the biopolymer cutin, as well as hydroxamate and hydrophilic moieties indicative of polysaccharides [1]. Traditionally found associated with inorganics, this represents a pivotal advancement in understanding Pu transport and biogeochemistry. Cutin biopolymers contain esters that can react with amines to incorporate nitrogen species [2]. This is one mechanism by which hydroxamate siderophores also present in soils at RFETS may be incorporated into organic matter, thus accounting for its high affinity for Pu.

The objective of this research was to isolate cutin from samples of Western wheatgrass (*Agropyron Smithii*), a dominant species of vegetation and likely contributor to soil organic matter at RFETS. The chemical isolation procedure [3] was modified and optimized to remove recalcitrant cellulose and lignin structures prevalent in grasses. Solid state ¹³C CPMAS NMR and two-dimensional HRMAS HSQC, TOCSY and COSY experiments were utilized to identify and characterize the isolated polymer.

Research results of the isolated material indicate the presence of crystalline and amorphous aliphatic long-chain polymethylenes containing esters, fatty acids, and primary and mid-chain hydroxy acids characteristic of cutin [3]. Also evident are residual carbohydrate/cellulosic material and aromatic groups in low but detectable quantities, reminiscent of the IEF extract containing Pu [1]. Thus it is likely that this biopolymer has contributed to the organic fraction of soil responsible for accumulating Pu and rendering it more mobile.

The interaction of cutin with deferoxamine, a tri-hydroxamate siderophore indicative of siderophores likely present in RFETS soils, and subsequent interactions with metals such as Pu and Fe are under investigation. These experiments along with analytical techniques such as ¹³C NMR, HRMAS, FTIR, etc., will further identify the molecular structure of wheatgrass cutin and clarify the role cutin may play in interactions with microbial siderophores and sequestering metals such as Fe and Pu in soils. This work fills an important gap linking the distinct sources of organic material in soils to their specific role in controlling the biogeochemical cycling of metals.

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Identification of Multiple Mercury Sources to Stream Sediments near Oak Ridge, TN, USA

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Sediments were collected and analyzed for total mercury concentration (THg) and mercury (Hg) isotopic composition from streams and rivers in the vicinity of the Y-12 National Security Complex (Y12) in Oak Ridge, TN. In the stream directly draining Y12 (East Fork Poplar Creek), where industrial releases of Hg have been documented, high THg (3.26 to 60.1 $\mu\text{g/g}$) sediments had a distinct Hg isotopic composition ($\delta^{202}\text{Hg}$ of $0.02 \pm 0.15\text{‰}$ and $\Delta^{199}\text{Hg}$ of $-0.07 \pm 0.03\text{‰}$; mean \pm 1SD, $n=12$). This was in contrast to relatively uncontaminated, low THg stream sediments in the region ($\delta^{202}\text{Hg} = -1.40 \pm 0.06\text{‰}$ and $\Delta^{199}\text{Hg}$ of $-0.26 \pm 0.03\text{‰}$; mean \pm 1SD, $n=6$). Additionally, several nearby tributaries that do not drain Y12 had sediments with intermediate THg (0.06 to 0.21 $\mu\text{g/g}$) and anomalous $\delta^{202}\text{Hg}$ (as low as -5.07‰). We suggest that the low $\delta^{202}\text{Hg}$ values in these sediments provide evidence for the contribution of an additional Hg source to sediments, possibly derived from atmospheric deposition. In sediments downstream of Y12 influence, this third Hg source is not discernible and the Hg isotopic composition can be largely explained by the mixing of low THg sediments with high THg sediments contaminated by Y12 discharges.

Illite spatial distribution regulates Cr(VI) adsorption capacity and kinetics

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This work examined how and to what extent illite spatial distribution regulates adsorption capacity and kinetics of Cr(VI) using column experiment and two-dimensional reactive transport modeling. Two sets of columns were packed with the same total amount of illite and quartz sand however in different spatial patterns. The two differs in the permeability contrast between the quartz and illite zones, with permeability ratios of 1.48 and 32.24 (sand over illite) for C columns (chemically heterogeneous) and PC columns (physically and chemically heterogeneous), respectively. Within each set, columns with different spatial patterns were set up: Mixed column (M), Flow-parallel column (FP), Flow-transverse column (FT1) and Flow-transverse 2 zones column (FT2). Flow-through experiments were carried out with acidic inlet solutions (pH = 4) containing Cr(VI) under the flow velocities of 0.6, 3.0, and 15.0 m/day.

Experimental results showed that illite spatial distribution strongly affects sorption capacity and kinetics, the extent of which depends on permeability contrast and flow conditions. Under the relatively low flow velocity of 0.6 m/day, the Cr(VI) curves of M and FT1 columns overlapped for both C and PC sets while the FP and FT2 columns show much longer tails. The average sorption rate increased with increasing flow velocities while the sorption capacity decreases with the increasing flow velocities. The largest difference were found between M PC and FP PC column at the low flow regime where FP PC column only had 13% of the sorption capacity and 6% of the sorption rates compared to the M PC column.

Reactive transport models that explicitly incorporate the exact mineral distribution were used to reproduce the data and to understand the mechanism. We further explored conditions with a wide range of the permeability-contrast and transverse dispersivity α_T , the two major variables that control sorption capacity and kinetics. The 2D modeling results showed that the adsorption capacity of FP column increases linearly with α_T , while the permeability-contrast showed negligible influence. For the FT2 column, however the capacity decreased linearly with permeability ratio. These observations provide valuable insights on key controls of mineral spatial structure controls on Cr(VI) fate and transport in the natural subsurface.

University-Led Research

Induced Polarization Signature of Biofilms in Porous Media: From Laboratory Experiments to Theoretical Developments and Validation

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We conducted three experiments to investigate the spectral induced polarization (SIP) source mechanisms in microbially active environments.

In the first experiment, we investigated the SIP response of different biofilm components. Our results show that: increasing cell concentration increases the imaginary conductivity (σ''); increasing the concentration of alginate decreases σ'' however, addition of bacteria cells causes an increase in σ'' ; increasing the phenazine (metabolite) concentration causes an increase in σ'' . This effect is enhanced in the presence of microbial cells; increasing the DNA concentration decreases σ'' . Addition of cells did not cause an increase in σ'' . Preliminary modeling suggests that in the absence of conductive biominerals the σ'' is a quantitative indicator of bacterial cell density.

In the second experiment, we examined the SIP response of common iron minerals associated with metabolic activity of microorganisms. Both pyrite and magnetite show high σ'' and real (σ') conductivities compared to hematite, goethite, and siderite. The σ'' spectra of both pyrite and magnetite exhibit a well-defined characteristic relaxation peak below 10 kHz, not observed with the other iron minerals. The σ'' of a mixture of iron minerals is dominated and linearly proportional to the mass fraction of the highly conductive (pyrite and magnetite) iron minerals. The σ'' magnitude increased with decreasing grain size diameter of magnetite and pyrite with a progressive shift of the characteristic relaxation peak towards higher frequencies. Our results suggest that SIP techniques can be used to track the formation of semi-conductive mineral phases such as pyrite and magnetite.

In the third experiment, we investigated biomineralization of iron minerals by *Geobacter sulfurreducens* and its Δ pilA mutant. Wild type (WT) and Δ pilA mutant cultures were supplemented with acetate, Fe citrate and elevated concentrations of phosphates. The WT and Δ pilA strains promoted the accumulation of Fe(II) and decrease of phosphate in the aqueous phase. While the WT favored the formation of structurally ordered flattened prismatic crystals, composed of O, P and Fe, resembling vivianite, the deposits recovered from Δ pilA culture had a similar elemental composition but its morphology was a rosette. The Fe/P ratio in the deposits recovered from the WT culture was higher than in deposits recovered from Δ pilA culture. The synthesis of vivianite by *Geobacter* is significant because vivianite has been shown to abiotically reduce U(VI). We anticipate characterizing the processes that control the biogeochemical cycling of iron and biogeophysical responses from porous media populated with iron reducing bacteria communities.

Isotopic Characterization of Biogeochemical Pools of Mercury and Determination of Reaction Pathways for Mercury Methylation

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This project utilizes stable Hg isotopes in the East Fork Poplar Creek (EFPC) watershed, TN to place new constraints on methylmercury (MeHg) production, transport and degradation. We seek to better understand mechanisms leading to decoupling of inorganic Hg and MeHg concentrations in the EFPC ecosystem. We are conducting ecosystem level studies of natural samples and experimental studies of Hg isotope fractionation. Natural samples have been collected from: wetland sediments and pore waters; stream sediments, surface waters and pore waters; stream bottom periphyton; and young-of-year stoneroller minnows and redbreast sunfish. We have: 1) completed three seasonal sampling campaigns and analyses of THg, MeHg, and isotopic composition of sediments, suspended particulates, surface waters, pore waters, and periphyton from EFPC, Hinds Creek and adjacent wetlands; 2) analyzed the isotopic composition of archived fish and invertebrate tissues obtained from the ORNL EA Group; 3) collected samples of dissolved gaseous mercury (DGM) from EFPC stream water, and 4) conducted photochemical and dark oxidation experiments with EFPC stream water to investigate Hg isotope fractionation.

Recently published results from this project show Y-12 impacted sediments have a distinct Hg isotopic composition that can be traced from EFPC to Poplar Creek and the Clinch River, and that the isotopic composition of Hg in sediments within the EFPC vary little along the flow path (Donovan, Blum, Demers, Gu, Brooks, Peryam, 2014, Environ. Sci. Technol. 48, 3666-3674). In contrast, additional analyses show that the Hg isotopic composition of total suspended solids and the dissolved phase within EFPC change with distance downstream. There are shifts in the average isotopic composition of Hg in suspended sediment (THgp) from Y-12 ($\delta^{202}\text{Hg} = -0.46\text{‰}$, $\Delta^{199}\text{Hg} = -0.03\text{‰}$) to downstream reaches ($\delta^{202}\text{Hg} = 0.08\text{‰}$, $\Delta^{199}\text{Hg} = -0.08\text{‰}$). Changes in isotopic composition of dissolved Hg (THgd) is less consistent across seasons and along the flow path. The isotopic composition of DGM ranged in $\delta^{202}\text{Hg}$ values from 0.97‰ to 1.10‰ and in $\delta^{199}\text{Hg}$ values from -1.52‰ to -0.29‰, differing significantly from that of stream water, suspended particulate matter, and sediments. Analyses of riparian wetland and hyporheic pore waters suggests that near-stream sources of Hg may be isotopically distinguishable from THgp and THgd within the stream channel. Analyses of biota suggest different isotopic compositions of MeHg and inorganic Hg in the stream ecosystem. Combining field measurements with experimental results we assess potential sources and processes driving changes in Hg concentrations and isotopic compositions along the EFPC flow path.

Reactivity of Iron-Bearing Phyllosilicates with Uranium and Chromium Through Redox Transition Zones

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Iron-bearing phyllosilicate minerals help establish the hydrogeological and geochemical conditions of redox transition zones because of their small size, limited hydraulic conductivity and redox buffering capacity. The bioreduction of soluble U(VI) to sparingly soluble U(IV) can promote the reduction of clay-Fe(III) through valence cycling. The reductive precipitation of U(VI) to uraninite was previously reported to occur only after a substantial percentage of clay-Fe(III) had been reduced. Using improved analytical techniques we show that concomitant bioreduction of both U(VI) and clay-Fe(III) by *Shewanella putrefaciens* CN32 can occur. Soluble electron shuttles were previously shown to enhance both the rate and extent of clay-Fe(III) bioreduction. Using extended incubation periods we show that electron shuttles enhance only the rate of reduction (overcoming a kinetic limitation) and not the final extent of reduction (a thermodynamic limitation). The first 20% of clay-Fe(III) in nontronite NAu-2 was relatively “easy” (i.e., rapid) to bioreduce while the next 15% of clay-Fe(III) was “harder” (i.e., kinetically-limited) to bioreduce and the remaining 65% of clay-Fe(III) was effectively biologically un-reducible. In abiotic experiments with NAu-2 and biogenic uraninite, 16.4% of clay-Fe(III) was reduced in the presence of excess uraninite. In abiotic experiments with NAu-2 and AH2DS, 18.5 to 19.1% of clay-Fe(III) was reduced in the presence of excess and variable concentrations of AH2DS. A thermodynamic model based on published values of the non-standard state reduction potentials at pH 7.0 (E'_H) showed that the abiotic reactions between NAu-2 and uraninite had attained apparent equilibrium. This model also showed that the abiotic reactions between NAu-2 and AH2DS had attained apparent equilibrium. The final extent of clay-Fe(III) reduction was well correlated to the standard state reduction potential at pH 7.0 (E°_H) of all of the reductants used in these experiments (AH2DS, CN32, dithionite, uraninite).

We also examined the reduction of nitrobenzene by CN32 in the presence of montmorillonite SWy-2 (low Fe(III) content) and nontronite NAu-2 (high Fe(III) content). Nitrobenzene and other nitroaromatic compounds (NACs) have been selected for study because their redox properties are well known and they have previously been used as redox probe molecules to examine the reactivity of clay-Fe(II). We found that the abiotic reduction of nitrobenzene became increasingly important as clay-Fe(II) accumulated in the system.

Inorganic Geochemical Controls on Neptunium Transport: Co-Precipitation in Minerals

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Neptunium-237, with a half-life of 2.14 million years, is a contaminant of concern for the U.S. Department of Energy. Multiple oxidation states are accessible, but under subsurface conditions of environmental importance the Np(V) oxidation state is strongly favored. This cation forms a linear dioxo cation, the neptunyl ion, which is soluble in aqueous solutions. Whereas it is tempting to assume that the Np(V) uranyl ion will behave similarly to the U(VI) uranyl ion in the subsurface, there are a variety of reasons to expect otherwise. Specifically, the Np(V)-O bonds within the neptunyl ion are weaker than those in the U(VI) uranyl ion, making the neptunyl ion O atoms more reactive. Also, the charge of the neptunyl ion is lower than that of the uranyl ion, which will impact charge balance mechanisms for co-precipitation reactions.

We hypothesize that the Np(V) neptunyl ion may be co-precipitated into a variety of low temperature mineral structures that form in the subsurface. The analogous situation has been demonstrated in several studies focusing on uranyl ions, but the only studies for neptunyl have examined calcite.

In order to derive a predictive understanding of Np(V) incorporation into a variety of minerals, we are experimentally examining incorporation of the neptunyl ion in several mineral phases that present different cation sites that are incorporation targets. The chosen mineral phases are part of the carbonate, sulfate, nitrate and borate families and contain either monovalent or divalent cations. Materials have been characterized by a variety of methods including inductively coupled plasma mass spectrometry (solution and laser ablation mode), UV-vis spectroscopy, X-ray photoelectron spectroscopy and time resolved laser fluorescence spectroscopy.

Results to date demonstrate both that incorporation of U(VI) and Np(V) in such structures differ significantly between the two actinyl ions, and also between structure types. We are thus bringing crystal chemical models to bear on the study of the local environments of incorporation.

Dominant Mechanisms of Uranium-Phosphate Reactions in Subsurface Sediments

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Phosphate addition is an in situ remediation approach that may enhance the sequestration of uranium without requiring sustained reducing conditions. However, the geochemical factors that determine the dominant immobilization mechanisms upon phosphate addition are insufficiently understood to design efficient remediation strategies or accurately predict U(VI) transport. The overall objective of our project is to determine the dominant mechanisms of U(VI)-phosphate reactions in subsurface environments. Our research approach seeks to determine the U(VI)-phosphate precipitates that form from homogeneous solutions, characterize the effects of phosphate on U(VI) adsorption and precipitation on smectite and iron oxide minerals, and investigate how phosphate affects U(VI) speciation and fate in field sediments.

Our initial studies investigated the products of U(VI)-phosphate reactions in the absence and presence of sorbing mineral phases. In homogeneous systems, autunites form even when other U(VI) phosphates are more thermodynamically stable. In the presence of Ca, U(VI) may also sorb to or coprecipitate with calcium phosphates. In heterogeneous systems, phosphate has no macroscopic effect on U(VI) adsorption to a smectite clay despite LIFS and EXAFS spectra showing a clear change in surface speciation. In contrast, phosphate enhanced U(VI) adsorption to goethite at pH 4 but suppressed adsorption at pH 6 and 8. For both smectite and goethite, autunites precipitated at high phosphate and U(VI) concentrations but only after a critical supersaturation was exceeded.

Our current activities focus on U(VI)-phosphate reactions in Rifle and Hanford site sediments. Synthetic groundwaters designed to match the major element compositions at the sites were employed for both sediment types. Batch studies show little to no U(VI) sorbs to Rifle sediments except at high (1 mM) phosphate concentrations. The addition of phosphate to the influent of columns of Rifle sediments results in substantial sustained decreases in effluent U(VI) concentrations. Sequential extractions of sediments from the columns confirmed the accumulation of uranium with time and observed a gradual shift of solid-associated uranium to less mobile species. EXAFS and LIFS analysis of these sediments suggested that U(VI) was immobilized by both precipitation of an autunite mineral and adsorption. Batch studies of Hanford sediments showed distinct behavior from the Rifle sediment system. Substantial U(VI) adsorption occurred and was enhanced by phosphate addition, with an autunite-type precipitate forming at initial U(VI) and phosphate concentrations above 25 μM and 100 μM , respectively. Ongoing column experiments are investigating U(VI) retention in Hanford sediments in the presence of phosphate.

Uranium fate in acidic waste-weathered sediments: Scaling of molecular processes to predict reactive transport

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Objectives: (1) Determine process coupling between mineral transformation and uranium speciation change in acid waste-weathered Hanford sediments; (2) Establish linkages between molecular-scale contaminant speciation and meso-scale contaminant lability, release and reactive transport; (3) Make conjunctive use of molecular- to field-scale data to constrain the development of a reactive transport model that includes contaminant sorption-desorption and mineral transformation reactions.

Hypotheses: (1) Reactive transport modeling of future U releases from the vadose zone of acid-waste weathered sediments can be constrained by combining information on contaminant bonding environment with quantification of contaminant phase partitioning and meso-scale kinetic data on contaminant release from the waste-weathered porous media; (2) Although field contamination and laboratory experiments differ in their diagenetic time scales, sediment and synthesized U minerals dissolution, neophase nucleation, and crystal growth reactions that occur during the initial system disequilibrium leave a strong imprint that persists with memory effects over subsequent longer-term equilibration time scales.

Research Approach: An iterative measure-model approach is applied to elucidate mechanistic underpinnings of reactive contaminant transport in weathering geomedia.

Experimental design: Crib waste simulants were reacted with Hanford sediments in batch and flow-through systems. Coupling of contaminant uptake to mineral weathering was monitored both during waste-sediment interaction, and after, when waste-weathered sediments are subjected to infusion with circumneutral background pore water (BPW).

Results: We completed bench-scale batch weathering to one year and flow-through column experiments where Hanford Sediments were reacted with U-bearing synthetic crib waste (SCW) solutions as a function of pH, U and phosphate concentrations. PO₄ exerted strong control over U speciation at all pH with rapid precipitation of meta-ankoleite [K(UO₂PO₄)•3H₂O] leading to near complete immobilization of U. Boltwoodite [K(UO₂)(HSiO₄)•1.5H₂O] increased even in PO₄-containing systems. Without PO₄, U speciation was controlled by the rate of silicate weathering. In this case, U immobilization was limited to 25-50% as precipitated becquerelite [Ca(UO₂)₆O₄(OH)₆•7H₂O] or compreignacite [K₂(UO₂)₆O₄(OH)₆•7 H₂O] and boltwoodite. Carbonate dissolution buffered influent solutions to pH ~?, which promoted silicate weathering and boltwoodite precipitation. Dissolution of synthetic compreignacite and Na-compreignacite yielded dissolution rates of 8.89•10⁻¹³ and 2.48•10⁻¹² mol m⁻² s⁻¹ (normalized to BET surface area), respectively. Desorption experiments of weathered sediments? revealed an incremental desorption of U for phosphate-free systems, indicating dissolution of compreignacite, becquerelite and schoepite, but solutions were saturated with respect to Mg-zippeite. In contrast, slow dissolution of meta-ankoleite and autunite in PO₄ systems showed low U release.

Bacterial Nanowires and Extracellular Electron Transfer to Heavy Metals and Radionuclides by Bacterial Isolates from DOE Field Research Centers

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Research conducted at the University of Southern California, Montana State University, and at Rensselaer Polytechnic Institute in Troy, New York, continues to embrace controlled cultivation technologies for evaluating the response of signature microorganisms to changes in environmental conditions. We are particularly interested in the activity and strategies invoked by attached microbial populations within highly-integrated "biofilm" communities.

Desulfovibrio vulgaris RCH-1 is a sulfate-reducing bacterium that was isolated from chromium-contaminated groundwater at the 100H Hanford Site. This organism formed biofilms under conditions of sulfate limitation at environmentally relevant temperature of 20°C. A variety of extracellular structures were observed by a variety of microscopic techniques. Apart from some metal deposits near the bacterial cell surface, metal precipitation occurred extracellularly predominantly on thin, elongated structures that in cross section appeared as stacks of membranous structures, or as complex geometrical enclosed shapes whose inside were always devoid of bacteria. Non-osmicated biofilms that were stained with a solution of uranyl acetate revealed an unstained thin core structure, which upon osmication becomes black, indicating that the thin structure is lipid-based. We also observed membrane vesicles nearby or docking to the extracellular structures, and these observations supported a membrane lipid-based origin. Serial section lipophilic dye FM1-43 in cryostat-sections revealed that the membrane structures persist for tens of micrometers. EDS imaging revealed presence of Fe, O and P, but not sulfide, and these results suggested the metal deposits are not solely the result of inorganic chemistry interactions of metals ions with hydrogen sulfide. The biofilm and metal deposition was visualized in 3D with SBF/SEM, and showed a heterogeneous distribution of metal precipitates away from cells. Assessing metal interactions at in situ temperatures in biofilms rather than optimal growth temperatures in bulk-phase and under electron donor- and acceptor-limitation with field isolates provides relevant insight into metal reduction for respective field sites.

Methods for visualizing the growth of extracellular structures in real time and under physiologically relevant and metabolically active conditions were developed by members of our extended team at USC and initially applied those methods to the facultative metal reducing bacterium *Shewanella oneidensis*. Recent results provide new insights into the strategies and components invoked for efficient extracellular charge transfer within electron acceptor-limited biofilms, many of which are consistent with observations made with *D. vulgaris* RCH-1. These approaches are currently being applied to the field isolate *Geobacter. daltonii* FRC32T using

Methods to Quantify Mercury Bioavailability in Sulfidic Sediments

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The production of methylmercury (MeHg) in the environment depends, in part, on the speciation of inorganic mercury and the portion that is available for uptake into methylating microorganisms. This research investigated two methods to quantify the bioavailable fraction of mercury in sediments and other settings relevant for MeHg production.

The first approach is a selective leaching protocol that utilized an anoxic leachate comprised of glutathione, a strong chelating ligand for Hg that may mimic sulfhydryl-containing ligands on the surface of methylating microorganisms. For a pre-defined leaching procedure (1 mM glutathione, 1 gram of sediment per 10 mL, and 0.5 h holding time), the results indicated a correlation between glutathione-leachable mercury concentrations and the native methylmercury concentrations in 10 different marine sediments. Further experiments were performed with anaerobic sediment microcosms that were amended with different types of Hg with a known variation in methylation potential. The glutathione-leachable mercury concentrations in these microcosms experiments also correlated to MeHg production. The results demonstrated that a thiol-based leaching protocol may be a more appropriate approach than other methods (e.g. tin-reduction, sequential extractions) for the determination of Hg bioavailability in sediments.

Because of the promising results of the glutathione-based leaching test, we explored the use of diffusive gradient in thin-film (DGT) samplers, a thiol-based passive sampler that can be used as an in situ method for Hg bioavailability. This method has been used previously to determine dissolved metal concentrations in water. However, when DGT samplers are deployed in sediment settings, it is unclear how the presence of small particles affects the performance of the samplers. To test this question, DGT samplers were exposed to solutions containing different formulations of HgS nanoparticles. The amount of Hg accumulated onto DGT was quantified and compared with the dissolved Hg(II) in the solution (quantified by 0.02- μ m filtration). The speciation of Hg on the resin layer was also identified by X-ray absorption spectroscopy. The results indicated that although the nanoparticles could not pass through the diffusion layer, they deposited on the surface of this layer and possibly clogged the pores of the sampler. As a result, the migration of dissolved Hg through the diffusion layer was retarded in the presence of the nanoparticles. Therefore, the Hg concentration predicted by DGT is smaller than the actual concentration in the bulk solution. The findings of our study have important implications for interpretation of Hg data obtained by DGT samplers in anoxic settings.

Fate of Uranium During Transport Across the Groundwater-Surface Water Interface

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Discharge of contaminated groundwater to surface waters is of concern at many DOE facilities. For example, at the Savannah River Site (SRS), uranium contaminated groundwater is discharging into natural wetlands. The numerous sharp biogeochemical transitions occurring in wetlands have profound effects on the ultimate fate of redox-sensitive trace metals and radionuclides, including uranium.

The goal of this research is to provide new insights on how plant-induced alterations to the sediment biogeochemical processes affect key uranium reducing microorganisms, uranium reduction, and uranium spatial distribution. We have formulated the following hypotheses. (1) U(VI) discharged from ground- to surface-waters can be immobilized effectively as U(IV) in the sediments at the groundwater-surface water interface. The electron donor required to stimulate the microorganisms capable of reducing U(VI) is provided by wetland plants via their root exudates and root turnover. (2) Oxygen released into the sediments by plants reoxidizes Fe(II), forming iron oxy(hydroxi)des, which provide the bioavailable Fe(III) for long-term bacterial iron-reducing activity, which is key for a sustained biological uranium reduction.

To test the above hypotheses, we operated small-scale wetland mesocosms to simulate the discharge of uranium-contaminated groundwater to surface waters. The mesocosms were operated for 80 days, followed by analysis for solid-associated chemical species, microbiological characterization, micro-X-ray fluorescence (μ -XRF) mapping of Fe and U on the root surface, and U speciation via X-ray Absorption Near Edge Structure (XANES).

Bacterial numbers including *Geobacter* sp., Fe(III), as well as total uranium, were highest on roots, followed by sediments near roots, and lowest in zones without much root influence. Results from the μ -XRF mapping on root surfaces indicated a strong spatial correlation between Fe and U, while the analysis via XANES showed that a significant fraction of uranium was reduced to U(IV), indicating that iron cycling in the rhizosphere also results in uranium reduction and immobilization. Under high iron loading, results indicate that co-precipitation of U(VI) with iron might have been an important U removal process.

A series of depth-discrete dialysis samplers were set up in an uranium-contaminated wetland on the SRS to monitor seasonal U dynamics. Vertical profiles of dissolved U are consistent with our laboratory findings, indicating that during the growing season when there is more active iron reduction, the dissolved U in the sediment pore water is significantly lower.

Integrated geophysical measurements for bioremediation monitoring: combining NMR, magnetic methods and SIP.

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Our research aims to develop borehole measurement techniques capable of monitoring subsurface processes, such as changes in pore geometry and iron/sulfur geochemistry, associated with remediation of heavy metals and radionuclides. Previous work has demonstrated that geophysical method spectral induced polarization (SIP) can be used to assess subsurface contaminant remediation; however, SIP signals can be generated from multiple sources limiting their interpretational value. Integrating multiple geophysical methods, such as nuclear magnetic resonance (NMR) and magnetic susceptibility (MS), with SIP, could reduce the ambiguity of interpretation that might result from a single method. Our research efforts will entail combining measurements from these methods, each sensitive to different mineral forms and/or mineral-fluid interfaces, providing better constraints on changes in subsurface biogeochemical processes and pore geometries significantly improving our understanding of processes impacting contaminant remediation.

The Rifle Integrated Field Research Challenge (IFRC) site was used as a test location for our measurements. The Rifle IFRC site is located at a former uranium ore-processing facility in Rifle, Colorado. Leachate from spent mill tailings has resulted in residual uranium contamination of both groundwater and sediments within the local aquifer. Studies at the site include an ongoing acetate amendment strategy, native microbial populations are stimulated by introduction of carbon intended to alter redox conditions and immobilize uranium. To test the geophysical methods in the field, NMR and MS logging measurements were collected before, during, and after acetate amendment. Next, laboratory NMR, MS, and SIP measurements were collected on columns of Rifle sediments during acetate amendment. The laboratory experiments were designed to simulate field experiments; changes in geophysical signals were expected to correlate with changes in redox conditions and iron speciation.

Field MS logging measurements revealed vertically stratified magnetic mineralization, likely the result of detrital magnetic fraction within the bulk alluvium. Little to no change was observed in the MS data suggesting negligible production of magnetic phases (e.g. magnetite, pyrrhotite) as a result of sulfidogenesis. Field NMR logging measurements maintained high levels of noise contamination requiring significant signal processing, and analysis suggests that any changes may be difficult to differentiate from simultaneous changes in water content. Laboratory MS and NMR measurements remained relatively stable throughout the course of the acetate amendment experiment, consistent with field measurements. However, SIP measurements changed during acetate amendment finding consistent with previous research indicating the formation of iron-sulfide mineral phases.

Identification of a c-type cytochrome involved in Mn(IV) reduction in *Anaeromyxobacter dehalogenans* strain 2CP-C

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Anaeromyxobacter dehalogenans strains are metabolically versatile Deltaproteobacteria that conserve energy from the reduction of a variety of electron acceptors, including insoluble manganese dioxide (MnO₂) and ferric oxides/oxyhydroxides (FeOOH). The goal of this research effort was to identify c-type cytochromes involved in electron transfer to the insoluble electron acceptor MnO₂.

The characterization of deletion mutants has revealed a number of c-type cytochromes involved in electron transfer to solid metal oxides in *Shewanella* spp. and *Geobacter* spp; however, knockout mutants often do not display distinct phenotypes indicating the limitations of this approach for making functional assignments to specific c-type cytochromes. A genetic system for *Anaeromyxobacter* is not available and functional assignment of c-type cytochromes is lacking. To identify *A. dehalogenans* c-type cytochromes involved in electron transfer to solid metal oxides, protein expression profiles of strain 2CP-C cells grown with acetate as electron donor and MnO₂, ferric citrate, ferric oxyhydroxide, nitrate or fumarate as electron acceptors were compared. Whole cell lysates were subjected to trypsin proteolysis and analyzed using liquid chromatography-tandem mass spectrometry (LC-MS/MS). Distinct c-type cytochrome expression patterns were observed in cells grown with the different electron acceptors. *A. dehalogenans* strain 2CP-C cells grown with insoluble Mn(IV) expressed 25 c-type cytochromes out of the 69 c-type cytochromes encoded on the strain 2CP-C genome. An uncharacterized c-type cytochrome (Adeh_1278) was uniquely expressed in strain 2CP-C cells grown with MnO₂. PCR and reverse transcriptase-qPCR demonstrated that the Adeh_1278 gene was transcribed in cells grown with MnO₂ but not with any of the other tested terminal electron acceptors. Apparently, the transcription of the Adeh_1278 gene and Adeh_1278 expression correlated with Mn(IV) reduction activity in *A. dehalogenans* strain 2CP-C. Adeh_1278 has three heme binding motifs and is predicted to occur in the periplasm. The identification of Adeh_1278 as a protein uniquely expressed during growth with MnO₂ suggests its utility as a biomarker for MnO₂ reduction and demonstrates the value of the LC-MS approach for making functional assignments to c-type cytochromes. The distinctive expression of c-type cytochromes in response to growth with different terminal electron acceptors offers opportunities for functional (i.e., activity) in situ monitoring using environmental metaproteomics or transcript-targeted approaches.

Going Wireless: Fe(III) Oxide Reduction without Pili by *Geobacter sulfurreducens* Strain JS-1

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Previous studies have demonstrated that the electrically conductive pili of *Geobacter sulfurreducens* strain DL-1 are essential for optimal extracellular electron transfer to Fe(III). *G. sulfurreducens* strain KN400 reduces poorly crystalline Fe(III) oxide more rapidly than strain DL-1. In order to further study the mechanisms for Fe(III) oxide reduction in KN400, the gene for PilA, the structural pilin protein, was deleted. Deletion of the PilA gene inhibited Fe(III) oxide reduction. However, slow rates of Fe(III) reduction were detected after extended (> 30 days) incubation in the presence of Fe(III) oxide. After seven consecutive transfers the adapted PilA-deficient strain, designated strain JS-1, reduced Fe(III) oxide as fast as the wild type. Microarray, proteomic, and gene deletion studies indicated that this adaptation was associated with greater production of the c-type cytochrome PgcA, which was released into the culture medium. Multiple lines of evidence suggested that PgcA acted as an electron shuttle, promoting electron transfer from the outer cell surface to Fe(III) oxides in strain JS-1. In contrast, PgcA was not required for effective Fe(III) oxide reduction in the wild-type strain. Strain JS-1 competed well with the wild-type strain when both were grown together on Fe(III) oxide. However, when 50% of the culture medium was replaced with fresh medium every three days, the wild-type strain out-competed strain JS-1. This result was attributed to the need for JS-1 to continuously replace the PgcA being removed from the medium, putting JS-1 at a competitive disadvantage, similar to the apparent selection against electron shuttle producing Fe(III) reducers in most soils and sediments. The long period necessary for the PilA-deficient strain of KN400 to adapt for effective Fe(III) oxide reduction, and the fact that deleting the gene for PgcA in the wild-type had no impact on Fe(III) oxide reduction, suggest that pili-mediated Fe(III) oxide reduction is more representative of the mechanism by which *G. sulfurreducens* reduces Fe(III) oxide in soils and sediments. The ability of KN400 to adapt to the loss of pili demonstrates that caution may be warranted in extrapolating to natural environments the mechanisms for Fe(III) oxide reduction elucidated in studies with cultures maintained for long periods under laboratory conditions that do not mimic those found in soils and sediments. The substantial plasticity encoded in the genomes of microorganisms capable of extracellular electron transfer, coupled with unnatural laboratory selection pressures, have the potential to lead to physiological responses that might not be found in natural environments.

SMART (Subsurface Microbial Activity in Real Time) Technology for Real-Time Monitoring of Subsurface Microbial Metabolism

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Real-time estimates of in situ anaerobic microbial activity are needed in order to elucidate the impacts of environmental perturbations, such as seasonal changes in temperature and nutrient availability, as well as to assess the effectiveness of bioremediation strategies. Current methods typically involve invasive sampling of the environment, which can alter microbial activities, and often require the addition of tracers and/or expensive analytical equipment, adding complexity and expense. Therefore, we developed SMART (Subsurface Microbial Activity in Real Time) technology as a novel approach to monitoring microbial metabolism in anaerobic sediments and submerged soils. The SMART approach is based on microbial fuel cell concepts that have previously been adapted to detect changes in the availability of relatively high concentrations of organic compounds in wastewater, or during in situ bioremediation of uranium-contaminated groundwater. However, in most soils and sediments, rates of microbial activity are not linked to the concentrations of organic substrates, but rather to the turnover rates of the substrate pools, which have steady state concentrations in the μM range. In order to determine whether levels of current produced at a graphite anode would correspond to the rates of microbial metabolism in anaerobic sediments, small graphite anodes were inserted at various depths in sediment cores and connected to graphite brush cathodes in the overlying water. Currents produced were compared with the rates of [2- ^{14}C]-acetate turnover because acetate is a central intermediate in the anaerobic degradation of organic matter, regardless of the predominant terminal electron-accepting process. Over a wide range of in situ metabolic rates, there was a direct correlation between current production and the rate that [2- ^{14}C]-acetate was metabolized to $^{14}\text{CO}_2$ and $^{14}\text{CH}_4$ in sediments in which Fe(III) reduction, sulfate reduction, or methane production was the predominant terminal electron-accepting process. At comparable acetate turnover rates, currents were higher in the sediments in which sulfate-reduction or Fe(III) reduction predominated than in methanogenic sediments. This was attributed to reduced products (Fe(II), sulfide) produced at distance from the anode contributing to current production in addition to the current generated from the microbial oxidation of organic substrates at the anode surface in all three sediment types. These results suggest that the SMART technology will serve as a simple, inexpensive, and effective approach for real-time monitoring of rates of anaerobic microbial metabolism in a diversity of anaerobic soils and sediments with applicability to the study of subsurface bioremediation and the impact of environmental perturbations on microbial activity.

Radiocarbon Signature of Microbial DNA from a Reducing Zone of a Floodplain aquifer, Rifle Colorado

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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 site 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 10³ filter housing and 0.2 μm 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±40 y. 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.,

Real-time, on-site and quantitative detection of bioavailable radionuclides and heavy metals in contaminated water at DOE sites

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Quantitative, real-time detection of radionuclides and heavy metal ions on-site remains a significant challenge while monitoring environmental resources such as groundwater and surface water. At the Integrated Field Research Center in Rifle, subsurface water contaminated with soluble and labile U(VI) is being converted to insoluble U(IV) by microbial action to fix the uranium and therefore an on-site sensor that can specifically quantify U(VI) in groundwater will provide a tool for monitoring uranium speciation and remediation progress.

Lu and coworkers have reported a DNAzyme based fluorescent uranium sensor with a detection limit of 11 ppt and high selectivity. It is specific for U(VI) as DNAzyme's are specific to a particular oxidation state of a metal. ANDalyze Inc. commercialized several DNAzyme based heavy metal sensors including sensors for uranium, lead, copper, zinc, cadmium and mercury using a combination of dry form sensor cartridge and a hand-held fluorimeter. The tests can be done in 2 minutes. The focus of our poster is the commercialized uranium sensor with a detection range of 2 - 60 ppb and a typical uranium recovery of 75-125% for field testing.

Previously, we collaborated with Ken Williams and Phil Long at Rifle and with Tonia Melhorn and Kenneth Lowe at ORNL to test our uranium sensor with samples from Rifle and ORNL sites. Twelve ORNL samples with ppm level uranium were analyzed after dilution and the results compared well to ICP (80-120% recovery). The Rifle samples had lower recovery of ~ 50%. We then optimized the protocol to test samples at Rifle which require a simple acidification to ~pH 5 prior to analysis by adding few drops of dilute acid. With the optimized protocol, we traveled to the Rifle site to perform field analysis of samples. Eight samples were analyzed using two each from plots A, B, C and D and the results compared to ICP. The samples had a uranium recovery of ~ 70-110% (compared to ICP results) which works well for quick, on-site field analysis. Since most samples showed a lower result than ICP, we are testing various uranium complexes that maybe found in the Rifle subsurface to test their effect on the sensor's ability to quantify U(VI) and therefore improving sensor performance.

To add capability of remote monitoring, we are currently in the process of developing a continuous monitor which will allow for unattended operations up to 30-days, while testing samples at a specified frequency.

Strikingly Different Form of Organic Carbon in Soils of Temperate and Permafrost Soils: Implications for Carbon and Metal Cycling

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Soils are major reservoirs of organic carbon (OC), and play a central role in the mobility of carbon between the land and the atmosphere. Among different soils, a significant fraction of global soil OC is stored in permafrost soils, and thawing and rapid losses of OC in the form of CO₂, associated with warming of polar regions, raises a serious concern for the stability of carbon in polar soils. Studies have shown that variations in soil mineralogy and biogeochemistry, and climatic conditions can modify the soil OC retention, which in turn alter the elemental cycles. The focus of our research is on how variations in vegetation and soil biogeochemical conditions control the dynamics of OC and associated major and trace elements in soils of different climatic conditions.

In this study, we examined OC forms associated with soils of temperate and polar climates using X-ray Absorption and NMR spectroscopic techniques, and high-resolution FT-ICR ESI-mass-spectrometry. In addition, to assess OC dynamics, we also evaluated the forms of S, P, and Cl bound to OC, and their time-dependent concentration variations. We compared the chemistries of these elements in Arctic soils with soils collected from temperate coniferous and deciduous forests.

Our studies indicate that the organic carbon is rich in lipids, and poor in aromatic and carboxylic carbon in the high Arctic soils when compared to soils of other climates. The O/C ratios of the extractable organic carbon also indicate that it is O-poor. This is in direct contrast to the organic matter found in soils of tropical and temperate climates, which is rich in lignins, tannins, and other condensed aromatics. The abundance of such a lipid-rich OC in high Arctic soils may be attributed to the moss, algae and fungal (or lichen) mats, whereas lignin and other aromatic-rich vascular plants are the common sources of OC in other climatic regions. Such a contrasting composition of OC in Arctic soils when compared to others suggests that these soils respond differently to temperature changes, and also interact differently with major and trace elements. We are evaluating how these different pools of OC modifies the cycling of nutrients, such as Fe, Mn, and the solubility and speciation of contaminants, such as Hg. A discussion on the contrasting forms of OC found in soils of different climates and their role in elemental cycles will be presented.

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

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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.

Quantification of actinide sorption enthalpies: Ongoing experiments have demonstrated that 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 Gibbs free energy increases with temperature. Thus, in all cases the endothermic reaction must be balanced by a positive entropy to yield a negative Gibbs free energy ($\Delta G = \Delta H - T\Delta S$). These measurements are consistent with the experimental hypothesis that removal of hydrating waters provides an entropically driven free energy of these sorption reactions. The increase in sorption as a function of temperature follows the trend, Th(IV) > U(VI) > Eu(III) > Np(V) which also corresponds to the effective ion charges and hydration energies of the given actinide oxidation states.

Examination of Pu redox speciation at solid water interfaces: 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. These experiments have been coupled with quantum mechanical calculations investigating the potential role of alpha radiolysis products, such as hydrogen peroxide (H₂O₂) and hydroxyl radical (•OH), in the reduction of Pu(V/VI) to Pu(IV). Preliminary results indicate that the OH radical readily reacts with water in the first hydration sphere instead of proceeding toward the electron density of the plutonyl. We have inferred that this reaction with a hydrating water transfers a hydrogen, creating a new •OH closer to the plutonyl. Ongoing work is examining the potential role of surface catalysis.

Examination of Pu aging and mineral incorporation: Desorption of ^{239/240}Pu aged 30+ years on SRS sediment was examined and found to be essentially irreversible. A "fresh" ²⁴²Pu tracer added during the desorption step did not exhibit the same behavior. Electron microscope and microprobe studies are examining the spatial distribution of Pu within these samples. The results from these experimental measurements are being compared with quantum mechanical calculations of actinide incorporation into pure mineral phases.

Using mercury-resistant bacteria to examine the effects of thiol complexation and thiol and Mer transporters on the microbial bioavailability of inorganic Hg and methylmercury

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Mercury bioavailability experiments were conducted using broad spectrum mercury-resistant strains of the bacteria *Pseudomonas stutzeri* and *Escherichia coli* that are capable of converting MeHg into inorganic Hg(II) and methane, and subsequently reducing Hg(II) to elemental mercury. These strains allowed us to quantify intracellular accumulation of Hg by monitoring the loss of volatile Hg(0) over short-term (hours) incubations. We used these strains to examine the bioavailability of thiol complexes of inorganic Hg and MeHg and the roles of thiol and Hg transporters in their uptake. Thiol complexation generally lowered intracellular uptake of inorganic and MeHg, but they were still bioavailable. We measured higher levels of Hg uptake in an *E. coli* strain with Hg transport proteins (MerT, MerE, and MerP) than in the same strain in which the genes for these transporters had been knocked out. However, there was no difference in Hg uptake rates for strains with or without functioning glutathione transporters. These results indicate that thiol-bound Hg is available to mercury-resistant bacteria and its uptake is facilitated by Mer transporters, but that glutathione transporters are not involved in the uptake of the Hg(GSH)₂ complex in *E. coli*.

Thiol complexes of MeHg (MeHg-cysteine and MeHg-glutathione) were bioavailable in mercury-resistant strains of *P. stutzeri* and *E. coli*. As was the case for inorganic Hg, when exposed to thiol complexes of MeHg, higher rates of intracellular accumulation of MeHg were observed in an *E. coli* strain with a functioning Mer transport system than in a strain in which genes for all three Mer transport proteins had been deleted. A similar level of suppression of MeHg uptake was observed in strains in which only the periplasmic component of the Mer transport system, merP, was knocked out, indicating a critical role for this protein in modulating the transport of thiolated-Hg into the cell. We conclude that the complexes MeHgOH and MeHg-cysteine are equally bioavailable to mercury-resistant bacteria, and that Mer transporters facilitate the uptake of MeHg.

Plutonium Immobilization and Mobilization by Soil Organic Matter

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Pu is believed to be essentially immobile due to its low solubility and high particle reactivity to mineral phase or natural organic matter (NOM). For example, in sediments collected from a region of SRS, close to a wetland and a groundwater plume, $^{239,240}\text{Pu}$ concentrations suggest immobilization by NOM compounds, as Pu correlate with NOM contents. Micro-SXRF data indicate, however, that Pu does not correlate with Fe. 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. Our results indicate that more Pu (IV) than (V) was bound to soil colloidal organic matter (COM), amended at far-field concentrations. Contrary to expectations, the presence of NOM in the F-Area soil did not enhance Pu fixation to the organic-rich soil, when compared to the organic-poor soil or the mineral phase from the same soil source, due to the formation of COM-bound Pu. Most importantly, Pu uptake by organic-rich soil decreased with increasing pH because more NOM in the colloidal size desorbed from the particulate fraction at elevated pH, resulting in greater amounts of Pu associated with the COM fraction. This is in contrast to previous observations with low-NOM sediments or minerals, which showed increased Pu uptake with increasing pH levels. This demonstrates that despite Pu immobilization by NOM, COM can convert Pu into a more mobile form.

$^{239,240}\text{Pu}$ concentrations are positively correlated to particulate hydroxamate (a type of siderophore) and nitrogen contents. In a previous study, almost all of the mobile $^{239,240}\text{Pu}$ in a soil sampled from near the contaminated 903 Pad in the Rocky Flats Environmental Technology Site (RFETS) was found to be associated with a macromolecule having cutin degradation products as the backbone, crosslinked to some hydrophilic moieties such as polysaccharides (to increase its solubility and thus mobility), hydroxamate, and amide functionalities (to chelate both Fe and Pu). The cuticle material from Western wheatgrass (*Agropythi Smithii*), one of the dominant vegetation species at the RFETS, was extracted, and carbohydrates removed from the crude cuticle extract. Oxidation and depolymerization experiments of cutin, incorporation of carbohydrates, siderophore compounds, as well as the chelation of Fe(III) (as a surrogate of Pu(IV)) during a simulated humification process, are assessed by ^{13}C NMR, HRMAS, ATR-FTIR, etc.).

Collaborative Research: The Importance of Organo-Iodine and Iodate in Iodine-127,129 Speciation, Mobility, and Microbial Activity in Groundwater at DOE Sites

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Iodine occurs in multiple oxidation states in aquatic systems in the form of organic and inorganic species (iodide and iodate). This fact leads to complex biogeochemical cycling of I and its long-lived isotope, ^{129}I , a major by-product of nuclear fission. In order to assess the distribution of ^{129}I and stable ^{127}I in environmental systems, a sensitive and rapid method was developed which enabled us to determine isotopic ratios ($^{129}\text{I}/^{127}\text{I}$) and speciate I via GC-MS and AMS. Results using this new method demonstrate that the mobility of ^{129}I species greatly depends on the type of I species and its concentration, pH, and sediment redox state, with equilibration times taking up to 12 weeks. At ambient concentrations ($\sim 10^{-7}$ M), I^- and IO_3^- are significantly retarded by sorption to mineral surfaces and covalent binding to natural organic matter (NOM), while at concentrations traditionally examined in sorption studies (i.e., 10^{-4} M or higher), I^- travels along with the water. Iodate removal can also occur through incorporation into CaCO_3 crystal lattice, e.g., at the Hanford Site. Iodide and iodate interactions with NOM lead to covalent binding of I to a limited number of aromatic carbon moieties on the particle surface. Iodine association with NOM is important in sediments, even when organic carbon content is very low (e.g., $<0.2\%$ at Hanford Site). A small fraction of NOM that is bound to iodine can behave as a mobile organo-I source, a process that we were able to numerically simulate using kinetic Michaelis-Menton-type redox-reactions and kinetic uptake reactions. Field and laboratory studies evaluating the cause for steady increases in ^{129}I concentrations (up to 1000 pCi L^{-1} , 3 orders of magnitude greater than drinking water limits of 1 pCi L^{-1} ^{129}I) emanating from radiological basins at the Savannah River Site (SRS) indicate that an increase of 0.7 pH units in groundwater over 17 years may explain the observed increased groundwater ^{129}I concentrations. Bacteria from a ^{129}I -contaminated aerobic aquifer at SRS were found to accumulate I^- at environmentally relevant concentrations (10^{-7} M), but likely do not account for the high fraction (up to 25%) of measured organo-I in groundwater. However, we found that microbial production of peroxy-carboxylic acids and superoxide radical facilitate iodide oxidation, forming reactive species (i.e. molecular iodine, hypo-iodous acid and tri-iodine) that could readily iodinate soil organic matter. A geochemical model accounting for iodine speciation transformations, NOM partitioning, and sediment sorption in the subsurface was developed.

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 uptake appears to be a result of accidental import during the acquisition of essential trace metals, such as Zn(II). While the mechanism of uptake is similar in methylating and non-methylating bacteria, the fate of the Hg(II) following its uptake is quite different. In the Hg methylating strains, *Geobacter sulfurreducens* and *Desulfovibrio* sp. ND132, methylmercury is produced in the cytosol and rapidly exported out of the cell. Thus the accumulation of Hg(II) in methylating organisms is offset by the export of methylmercury. In contrast, *Shewanella oneidensis* does not produce methylmercury, and this is reflected in higher Hg(II) accumulation rates and yields as compared to other methylating strains. Despite the lack of methylation, however, cells of *S. oneidensis* appear to export Hg(II) possibly as a complex with a thiol such as glutathione. The export of Hg(II) or methylmercury in these different bacteria may represent metal homeostasis mechanisms to deal with the accidental uptake of toxic heavy metals such as Hg(II) at sub-toxic concentrations, where the mer-mediated Hg resistance pathway is not necessary.

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

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Fe-bearing clay minerals serve as an important source and sink for electrons in redox reactions in various subsurface geochemical environments. Heterogeneous reactions between aqueous Fe(II) and Fe(III) oxides have been extensively studied, leading to a new conceptual framework which includes electron transfer between Fe(II) and structural Fe(III), bulk electron conduction, and Fe(II)-Fe(III)oxide atom exchange. Reactions of aqueous Fe(II) with clay minerals have received much less attention and are often described in terms of surface reactions including ion exchange, surface complexation, and/or surface precipitation. Our objectives here are to:

3. Determine if electron transfer occurs between sorbed Fe(II) and structural Fe(III) in clays over a range of conditions and clay structures.
4. Evaluate whether Fe atom exchange occurs between aqueous Fe(II) and structural Fe(III) in clays, and natural, clay-rich sediments.

We have investigated Fe electron transfer and atom exchange in clay minerals via selective chemical extractions, Fe isotope experiments and computational molecular modeling. Our findings indicate that structural Fe(III) in two nontronite clay minerals (NAu-1 and NAu-2), as well as a montmorillonite clay mineral (SWy-2) is reduced by aqueous Fe(II) and that electron transfer occurs when Fe(II) is sorbed to either basal planes and edge OH-groups of clay mineral NAu-1. Significant electron transfer occurred from edge OH-group bound Fe(II) at pH 7.5. At pH 4.0 and 6.0, where Fe(II) is sorbed primarily to the basal planes, electron transfer still occurred but to a much lower extent than from edge-bound Fe(II). Interestingly, the greatest extent of reduction was observed in the SWy-2 montmorillonite which contains the lowest % by weight Fe (2.8%). Findings from highly enriched isotope experiments suggest that between 5 and 20% Fe atom exchange is occurring between aqueous Fe(II) and structural Fe in a clay mineral. Experiments with higher precision isotope measurements using the multi-collector ICP-MS at Wisconsin confirm these findings. First principles calculations using a small polaron hopping approach suggest surprisingly fast electron mobility at room temperature in nontronite consistent with temperature dependent Mössbauer data. Electron conductivity of bulk nontronite is predicted to be highest through the octahedral sheet, as opposed to the tetrahedral sheet or from the tetrahedral to the octahedral sheet.

Geochemical zonation linked to microbial spatial distribution and microbe-mineral interactions in metal-immobilizing systems

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Recent developments in microbial community sequencing and visualization techniques enable analyses of biogeochemical zonation and microbe-metal interactions at an unprecedented detail when combined with advanced geochemical analysis and redox chemistry mapping techniques. To this end, a series of SRBRs containing solid organic substrate at different ratios have been established to query the biogeochemical zonation of microbe-mineral interactions associated with zinc immobilization. Our approach, which integrates Illumina sequencing, species-specific metallo-labeling of microbial cells and detailed synchrotron and microscopic geochemical analyses, was used to establish correlations between microbial populations and geochemical reactions.

Examination of the sulfate-reducing clades in pilot-scale systems that effectively immobilized soluble Zn revealed that the genera *Desulfosporosinus* and *Desulfurispora* coincided with high Zn-removal. In contrast, systems where the major sulfate-reducers were related to *Desulfosporomusa* consistently removed less Zn. Preliminary data also suggest that a similar pattern wherein phylogenetic affiliations serve as indicators for metal immobilization may exist for key cellulose degraders, such as *Dysgonomonas* that were negatively correlated with Zn-removal in these systems.

After approximately eight months of operation, Zn-removal was situated in the upper portions of the down-flow columns followed by a trend of downstream migration after twelve months. Canonical correspondence analysis revealed that Zn-removal was positively correlated with organic substrates containing alfalfa hay, whereas the opposite was shown for columns containing woodchips. A combined approach using scanning-electron microscopy and energy dispersive X-ray spectrometry to analyse column substrates revealed preferential associations of Zn and S in those that more effectively removed Zn over a period of one year. Further investigation employing synchrotron-based X-ray absorption spectroscopy (μ XAS) is underway in order to analyze sulfur speciation and provide 2-D redox mapping of precipitates on beamline 14-3 at the Stanford Synchrotron Radiation Lightsource.

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) has been 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. We have confirmed that our improved protocol works well for *Escherichia coli*, *Shewanella oneidensis* and *S. putrefaciens*, the latter two are all known metal-reducers and thus highly relevant in a contaminant mobility context. Efforts are currently focused on visualization of the microbe-metal interface through Gold-FISH labeling of *Shewanella* cells in the presence of manganese oxide (Birnessite) and subsequent μ XAS analysis.

238U/235U as an indicator of re-oxidation of U(IV) in the subsurface of remediated sites

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At the controlled field setting at the Rifle, CO IFRC site, acetate-induced biostimulated reduction of U has been demonstrated to be accompanied by large variations in 238U/235U (discussed as $\delta^{238}\text{U}$). Under both iron reducing and sulfate reducing conditions, 238U is preferentially reduced to U(IV), leaving the remaining groundwater U(VI) relatively enriched in 235U with shifts in the $\delta^{238}\text{U}$ of ~ 1.3 and -1.9‰ , respectively, for a $>90\%$ apparent U(VI) loss.

The long-term success of biostimulation as a remediation technique depends on the stability of sequestered U(IV). Uranium is readily oxidized by dissolved oxygen (DO) and other oxidants, such as nitrate, MnO₂, and ferrihydrite, posing a problem for long-term bioremediation efficacy. Because reduction of U(VI) deposits isotopically heavy U(IV), remobilization of this U(IV) has the potential to be detected when this isotopically heavy U is added back into the dissolved U(VI) pool. To assess changes in U concentration and 238U/235U accompanying re-oxidation, we present the results for two Rifle IFRC field re-oxidation experiments with dissolved oxygen (DO) and nitrate as the oxidants.

In both experiments, an oxidant (i.e., DO or nitrate) was injected into a previously biostimulated plot. Both DO and nitrate injections led to U concentration increases (up to 270 and 558 ppb, respectively), well above that of inflowing upgradient groundwater (~ 175 ppb). For the DO injection, U concentration increases were accompanied by a significant increase in $\delta^{238}\text{U}$ from -0.60‰ to 0.00‰ , possibly indicative of re-oxidation of isotopically heavy U(IV). However, despite the clear increase in the $\delta^{238}\text{U}$, re-oxidized U(IV) cannot be identified definitively as the source because the DO injection experiment began during the time the experimental plot was recovering from acetate-induced reduction (i.e., the $\delta^{238}\text{U}$ was still isotopically lighter than upgradient groundwater). However, the nitrate injection reveals for the first time a significant increase in $\delta^{238}\text{U}$ from $\sim 0.00\text{‰}$ to 0.50‰ , well above that of upgradient water (0.02‰). This clearly indicates re-oxidation of isotopically heavy U(IV) as hypothesized.

Our research demonstrates the potential for 238U/235U measurements to detect re-oxidation of previously sequestered isotopically heavy U(IV) in the subsurface and to distinguish between U(VI) additions from re-oxidation and other processes such as desorption. These results contribute to the development of 238U/235U as a powerful tool in the assessment of the effectiveness of U bioremediation efforts.

Identifying Components of Toxic Metal Stress and Hg Methylation with Global Proteomics

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We study *in vivo* and *in vitro* modifications of proteins by organic and inorganic mercury compounds, specifically:

INORGANIC Hg(II) EXPOSOME OF A NON-METHYLATING GAMMA PROTEOBACTERIUM: The inorganic-Hg(II) exposome of the model bacterium *E. coli*, reveals a large decrease in modifiable protein cysteines as measured by iodoacetamide (IAM)-induced carboxyamidomethyl (CAM)-modifications (also seen previously in organo-Hg exposure). Surprisingly, few proteins had detectable Hg(II)-adducts and all that did had at least two cysteines in the same peptide, affording strong chelation of Hg(II). Hg(II) exposure produced more unmodified cysteines than PMA exposure, suggesting biologically-formed Hg(II)-adducts may have been lost during MS analysis. Regardless of whether this differential observation of organic- and inorganic-Hg adducts occurs biologically or during analysis, it reflects a chemical difference in these ligands with potential biological implications. We're pursuing this question in well defined pure proteins and peptides (below).

INORGANIC Hg(II) EXPOSOME OF A METHYLATING SULFATE-REDUCING BACTERIUM: *Desulfovibrio* ND132 growing facultatively with or without Hg(II) exhibited 54% of 3455 encoded proteins. Unlike the *E. coli* observations, we saw no change in (CAM)-modifications or unmodified protein cysteines with or without Hg(II). Remarkably, we observed no Hg(II)-modified proteins with or without IAM, perhaps because some of the 1 mM cysteine in the medium was metabolized to H₂S, thus sequestering Hg(II) as insoluble HgS. Since ND132 methylates Hg(II) under these conditions, HgS may be the direct substrate for HgcAB or unidentified proteins may transfer Hg(II) from HgS to HgcAB. Possible candidate metallochaperones are being screened genetically.

LC-MS/MS OBSERVATION OF RHg- VERSUS Hg(II)-MODIFICATIONS: Differences in proteomic detection of Hg- and RHg-adducts could arise from differences in formation during cell exposure or in stability to LC-MS/MS processing. Such differences could underlie documented differential toxicity and bioaccumulation of these compounds, impacting remediation and stewardship. We found a pure synthetic peptide PMA-adduct stable over a range of MS inlet temperatures and voltages but its signal was 10-fold less than the unmodified peptide. With two well defined cysteine-rich proteins [the secreted enzyme lysozyme, (8 cysteines as disulfides) and the metalloregulator MerR, (8 cysteines as thiols)], we found that: (a) the most readily reduced lysozyme disulfides are highly modified by PMA or Hg(II); (b) either modification occurs less than CAM-adducts in the same peptide; and (c) PMA yields more adducts than Hg(II). These simple systems mimic proteomic results and will aid in defining the differential detectability/stability of organic and inorganic Hg-protein adducts.

Mineral Solubility and Free Energy Controls on Microbial Reaction Kinetics: Application to Contaminant Transport in the Subsurface

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Traditional kinetic and thermodynamic models incorporating microbial processes are typically developed using data from batch reactors in nutrient rich media characterized by rapid microbial growth, high respiration rates, and high cell densities. In the subsurface, however, microbial communities survive under energy and nutrient limiting conditions resulting in slow to zero growth conditions that cannot be reproduced by conventional kinetics. In this project, new rate laws able to predict microbial respiration in natural conditions are developed using two approaches. First, microbial growth under bioenergetic limitations is simulated using a novel flow-through bioreactor designed to include a retention filtration unit (retentostat) and accumulate biomass over time. Maintenance energy requirements for dissimilatory reduction of nitrate, a common groundwater contaminant, were determined by running the retentostat under limited conditions with lactate as electron donor. Initial rates of ammonium production by *Shewanella oneidensis* as model microorganism were similar in the bioreactor and otherwise identical incubations conducted in batch reactors. ATP measurements, however, showed slow yet increasing microbial growth over time in the retentostat while cells in the batch reactors did not grow significantly and died within 2 weeks of inoculation. In a second approach, rates of enzymatic U(VI) reduction were measured under variable, but controlled, geochemical conditions to determine the effect of uranyl speciation on bioreduction rates by *S. putrefaciens* as model metal-reducing microorganism. High pH, DIC, Ca²⁺, and Mg²⁺ suppressed the formation of labile U(VI) complexes and retarded uranium bioreduction. These results indicate that the main reducible fraction of U(VI) consists of non-carbonate complexes despite being the least abundant species in solution. At elevated concentrations of bioavailable uranyl species, however, bioreduction was inhibited by the toxicity of uranium to cells. Viability assays confirmed that the 'free' uranyl ion is responsible for uranium toxicity to *S. putrefaciens*, in agreement with the biotic ligand model of metal toxicity. A U(VI) bioreduction rate law that accounts for the speciation of U(VI) species is able to reproduce bioreduction rates in all pH, carbonate, calcium, and magnesium conditions. Future retentostat experiments will be designed to examine the thermodynamic controls on the bioreduction of non-carbonate U(VI) species in the presence of alternative electron acceptors. The kinetic and thermodynamic parameters determined in the current study will be directly applicable in reactive transport models to predict the rates of microbial respiration in both natural and contaminated subsurfaces.

Survival During Long Term Starvation: Global Proteomics Analysis of *Geobacter sulfurreducens* Under Prolong Electron Acceptor and Donor Limitation

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The dissimilatory iron-reducing anaerobe *Geobacter sulfurreducens* is used as a model organism for understanding bioremediation at contaminated subsurface sites. In our studies, *G. sulfurreducens* has been shown to exhibit a GASP phenotype in the laboratory, and to revive from long-term starvation (>500 days) when inoculated into fresh medium. Upon revival, the cells are capable of reducing Fe(III) in Fe citrate. These studies have been aimed at elucidating the mechanisms employed by *G. sulfurreducens* for such long-term survival, under both electron donor and terminal electron acceptor (TEA) conditions, the latter of which could exist after prolonged carbon addition at bioremediation sites.

To investigate potential changes in protein/enzyme expression under nutrient-limited conditions, global comparative proteomics analyses were carried out for *G. sulfurreducens* cultures in mid-log and survival phases. Cultures were grown under both acetate (electron donor)-limited and fumarate (TEA)-limited conditions, and proteins were harvested at mid-log and long-term survival time points. The proteins were analyzed by LC/MS-based iTRAQ methods, and those peptides which exhibited changes in abundance between mid-log and survival phases at a significance level $p < 0.05$ were further analyzed to determine function and cellular location. Under both electron donor- and TEA-limited conditions, many of the proteins up-regulated in survival phase vs. mid-log phase were involved in energy metabolism, and were membrane-associated. In contrast, many proteins involved in anabolic processes were down-regulated under nutrient-limited conditions. Other up-regulated proteins included those involved in protein transport, indicating that the cells are poised to sense nutrients in the environment as they become available.

Changes in acetate, fumarate, and succinate were monitored by HPLC under both acetate (electron donor)-limited and fumarate (TEA)-limited conditions to document points at which the cultures became nutrient-limited. Under acetate-limited conditions (5.5 mM acetate/30 mM fumarate), acetate was completely depleted within 3 days, while fumarate depleted rapidly within 3 days to ~12 mM, then continued to decrease gradually over ~75 days, with concomitant accumulation of succinate to ~25 mM. Under fumarate-limited conditions (30 mM acetate/50 mM fumarate), fumarate was depleted by day 7, during which time succinate concentrations increased then leveled off at ~50 mM, while acetate concentrations decreased to ~15 mM by day 3 and did not change thereafter. These results indicate that when the cells are electron-donor (acetate) limited, they may utilize other, less favorable intracellular or environmental electron donors as necessary. However, when TEA-limited, the cells survive in a highly reduced state until new electron acceptors become available.

Microbiological-enhanced mixing across scales during in-situ bioreduction of metals and radionuclides at Department of Energy Sites

Albert Valocchi (valocchi@illinois.edu) - University of Illinois, (PI); Charles J. Werth; Wen-Tso Liu; Robert Sanford; (University of Illinois) (Co-PIs).

Bioremediation is being investigated for long-term management of DOE sites contaminated by metals and radionuclides. Bioremediation typically requires injection of chemicals into the subsurface which mix at varying scales with the contaminant to stimulate the growth of dissimilatory metal reducing bacteria (DMRB). These bacteria couple the oxidation of injected chemicals to the reduction of contaminants as they mix in the groundwater. Syntrophic interactions with other bacterial species may also be exploited to supply DMRB with higher quality electron donors such as H₂ that are otherwise difficult to deliver to bacteria. Evidence from DOE field experiments suggests that mixing limitations of substrates at all scales may affect biological growth and activity for reduction. We are investigating this phenomenon using batch and microfluidic experiments and mathematical modeling.

In order to elaborate and investigate the energy transfer from an obligate symbiont, syntroph, to a partnering metal-reducing organism, we set up a two-species culture of *Syntrophobacter wolinii* DB and *Geobacter sulfurreducens*. Two strains of *Geobacter sulfurreducens* were successful partners: PCA (type strain) and KN400 (strain producing more nanowires than average). In contrast, a *G. sulfurreducens* PCA hydrogenase mutant could not serve as a partner. Therefore, hydrogen likely served as an electron shuttle between *S. wolinii* DB and *G. sulfurreducens*.

We successfully fabricated nanofluidic reactors designed to investigate the ability of bacterially produced conductive pili, or 'nanowires', to enhance the zone of mixing beyond what is possible by advection and dispersion alone. Our microfluidic experiments have identified realistic flow parameters and growth conditions amenable for growth and attachment inside these reactors that will be used in nanofluidic experiments.

A microfluidic reactor with an idealized porous medium geometry was used to study the metal reduction and biofilm grown at the pore scale. Selenite (a representative metal and an electron acceptor) and propionate (an electron donor) were delivered through the inlets and mixed along the centerline by transverse diffusion. Selenite was biologically converted to three different precipitates (monoclinic selenium, trigonal selenium, and selenium sulfide), and were segregated in the mixing zone. A continuum-scale model was developed and explained the segregation.

Our future work focuses on evaluating electron transfer across a nanoporous barrier using the two-species syntroph / *Geobacter* culture in order to elucidate electron transfer mechanisms, and on modeling this process in more realistic pore-scale geometries. We are also developing a hybrid multi-scale modeling framework to allow accurate representation of localized biofilm reactions in field-scale models.

Long-term uranium sequestration as nitrate invades a previously reduced zone - DOE Oak Ridge IFRC site

Weimin Wu (billwu@stanford.edu) - Stanford University, Craig S. Criddle (PI).

W.-M. Wu, C. Criddle- Stanford University, D. Watson, T. Mehlhorn, K.Lowe, J. Phillips, J. Earles, G.-P. Tang- Oak Ridge National Laboratory, B. Li, Y.-Q. Chao, T. Zhang- The University of Hong Kong, D. H. Phillips- Queen's University of Belfast, S.D. Kelly-EXAFS Analysis, P.-S.Li, H.-C.Tao-Peking University Shenzhen Graduate School, Z.-B. Chen- Dalian Nationalities University. A long term pilot-scale study of in-situ U(VI) sequestration was conducted at a site at the U.S. DOE Y-12 National Security Complex, Oak Ridge, TN. The contaminated sediments contained up to 5-6% of iron and 700-1000 mg U/kg dry weight with groundwater U of ~20-40 mg/L. U concentrations lower than the US EPA MCL (0.03 mg/L) were achieved through bioreduction treatments using intermittent injection of ethanol. Since the end of the bioreduction study, we have examined the long-term effect of exposure of the bioreduced sediments to nitrate from the natural influx of contaminated groundwater for > 1,500 days. Vertical and horizontal spatial differences in the increase (recovery) of U concentration and biogeochemical response to the influx of groundwater were observed. In general, the nitrate concentrations in the previously bioreduced area increased gradually from near zero to ~50-300 mM and then stabilized. The pH declined from the bioreduced levels of 6.2-6.7 to below 5.0. U concentrations in the bioreduced zone typically rebounded, declined and then rebounded again. The U(IV) in sediments was reoxidized to U(VI) species according to XANES analysis but the Uranium content in the sediment remained as high as previously identified. SEM-EDX analysis of reoxidized sediment samples revealed clusters of U containing carbonate precipitates (~1-2% U, w/w) that also contain high amounts of Fe, Al and Si, indicating that at least some U was still sequestered in-situ after the reintroduction of contaminated oxic groundwater. Significant levels (>100000 ppmv) of N₂O was found in groundwater after reoxidation. The impact of geochemical change on subsurface microbiology was investigated by 454 pyrosequencing analysis of the sediment samples. Significant community shifts occurred after the re-oxidation. The bioreduced communities dominated by sulfate-reducing (*Desulfovibrio*) and iron reducing (*Geobacter* and *Geothrix*) bacteria shifted to denitrifying *Rhodanobacter*, iron(II) oxidizing *Phizomicrobium* as well as denitrifying *Castellaniella* under more oxic conditions. However, the U(VI)-reducing, spore-forming sulfate reducing bacteria, *Desulfosporosinus* remained abundant under the oxic conditions. These observations indicate significant U sequestration continued after the oxidative agent nitrate invaded the bioreduced area.

Hg(0) oxidation by Anaerobic Bacteria

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Background and Objectives: Redox cycling between elemental [Hg(0)] and divalent [Hg(II)] mercury is a key control on the fate and transport of Hg in groundwater systems. Whereas dissolved gaseous elemental mercury [Hg(0)] is mobile in groundwater, while oxidized mercuric mercury [Hg(II)] readily sorbs onto mineral surfaces and organic matter. The objectives of this study were: 1) to determine if anaerobic bacteria catalyzes the oxidization of Hg(0) to Hg(II); and 2) to determine anaerobic Hg-methylating bacteria produce MeHg when provided with Hg(0) as the sole Hg source.

Research Methods: Hg(0) oxidation experiments were carried out with the obligate anaerobic bacteria *Geothrix fermentans* H5 and *Desulfovibrio desulfuricans* ND132 and the facultative anaerobic bacteria *Shewanella oneidensis* MR-1 and *Cupriavidus metallidurans* AE104. To demonstrate the formation of Hg(II), we performed ethylation experiments and X-ray absorption near edge structure (XANES) spectroscopy on Hg(0)-reacted cell. Finally, samples from experiments conducted with the methylating bacterium strain ND132 were analyzed for the production of MeHg.

Results: All four bacterial strains reacted with dissolved gaseous Hg(0) to form non-purgeable Hg. Derivatization of non-purgeable Hg to diethylmercury and the Hg LIII-edge position of the XANES spectra demonstrated that the Hg(0)-reacted bacterial samples had formed oxidized Hg(II). XANES analysis also revealed that cell-associated Hg(II) was covalently bound to bacterial functional groups, most likely to thiol moieties. Experiments with metabolically active and heat-inactivated cells indicated that both live and dead cells oxidized Hg(0) to Hg(II). MeHg analyses showed that live cells of *D. desulfuricans* ND132 produced large quantities of methylmercury. The results of this work demonstrate a potentially important pathway in the mercury cycle, whereby anaerobic bacteria produce MeHg when provided with dissolved Hg(0) as their sole Hg source.

TES Poster Abstracts

Ameriflux

Understanding Interannual Variability of Long Term Flux Measurements over Oak Savanna and Annual Grassland

Dennis Baldocchi (baldocchi@berkeley.edu) - University of California, Berkeley (PI), Siyan Ma (co-author) (Co-Pi).

We have been measuring carbon and water fluxes over an oak savanna and annual grassland in California since 2001. We present data on the year to year variability of these fluxes. Year to year variability remains large. The past two years are especially noteworthy, as during the 2013 drought it quit raining after January and we received less than 350 mm of rain. This year, spring leaf out occurred 10 days earlier than normal. We continue to explore reasons for interannual variability in fluxes and are looking at the roles of lags and leads between fluxes and environmental and ecological drivers.

AmeriFlux Management Program QA/QC Technical Team

Sebastien Biraud (scbiraud@lbl.gov) - Lawrence Berkeley National Laboratory (PI), Stephen Chan 1, Chad Hanson 2, David Billesbach 3, and Margaret Torn 1; 1: Lawrence Berkeley National Laboratory; 2: Oregon State University; 3: University of Nebraska, Lincoln (Co-Pis).

The goal of AmeriFlux is to develop a network of long-term CO₂ flux sites for quantifying and understanding the role of the terrestrial biosphere in global climate change. The network currently includes more than 100 sites started by many scientists and supported by multiple agencies (DOE, NSF, USDA, NFS). The AmeriFlux Management Program (AMP) Technical QA/QC at LBNL strengthens the entire Ameriflux Network and Core Sites by: (1) standardizing operational practices, calibration, and maintenance routines; (2) setting clear data quality goals, and (3) helping resolve instrument failure promptly. To ensure inter-comparability in the network, we conduct site comparisons with portable eddy covariance (PEC) systems, provide calibration gas standards and lab-quality sensors to check instrument performance, and identify uncertainties associated with data processing using data diagnostics and gold-standard files. During the past year, the LBNL AmeriFlux QA/QC lab transitioned from the AmeriFlux QA/QC lab at Oregon State University (OSU). In particular we built two new PEC systems. Our team is experienced in testing new instruments and working with manufacturers, and is building relationships with both vendors and investigators. We have completed eight site visits in 2013, and are planning eight site visits in 2014.

Connecting ecosystem carbon observatories in Europe and USA - the COOPEUS project and the ICOS infrastructure

Dario Papale (darpap@unitus.it) - ICOS ETC - University of Tuscia, Viterbo (ITALY), (PI).

The COOPEUS project (www.coopeus.eu), funded under the 7th Framework Programme for Research and Innovation of the EU, has the aim to bring together scientists and users being involved in Europe's major environmental related research infrastructure projects with their US counterparts, starting from the one funded by NSF.

The intention is that by interlinking these activities new synergies are generated that will stimulate the creation of a truly global integration of existing infrastructures. The keys of this integration process will be the efficient access to and the open sharing of data and information produced by the environmental research infrastructures and the harmonization and standardization of methods, protocols and data products.

In Europe the Integrated Carbon Observation System (ICOS - www.icos-infrastructure.eu) infrastructure is going to monitor atmospheric, ecosystem and ocean carbon and GHGs concentrations and fluxes across the continent, under the coordination of Thematic Centers that will ensure standard methodologies and processing. The Ecosystem Thematic Center, coordinated by Italy with a contribution from Belgium and France, is developing standard protocols to acquire and process data from more than 60 sites in Europe all equipped with eddy covariance systems to measure atmosphere-ecosystem exchanges of CO₂, CH₄, N₂O, water and energy.

In this initial phase of the infrastructure where the methods and products are defined, it is crucial to interact, discuss and harmonize the activities between ICOS and similar initiatives in USA. This is ongoing with both the National Ecological Observatory Network (NEON) and the AmeriFlux networks with exchange of information, common initiatives, protocols comparison and tools development. Increasing the level of harmonization and comparability will simplify global use of our data and will be an example also to the others emerging networks worldwide.

In this poster the ICOS ecosystem infrastructure and the ongoing coordination activities and exchanges with the NEON and AmeriFlux initiatives will be presented with a special emphasis on the next future COOPEUS actions, with the aim increase the participation to the discussion level in the communities.

AmeriFlux Data Collection, Processing, and Data User Support

Gilberto Pastorello (gzpastorello@lbl.gov) - Lawrence Berkeley National Laboratory, Margaret Torn (PI), Deb Agarwal (project leader); Dario Papale; Cristina Poindexter; Boris Faybishenko; Tom Boden; (Co-PIs).

The AmeriFlux Data Management team is providing new and expanded services. These services include: archiving of high frequency data from sites; high frequency data processing; enhanced quality assessment capabilities; advanced data processing capabilities; improved biological, ancillary, disturbance, and metadata collection methods; and expanded user services available via the AmeriFlux web site. The Data Management team and accomplishments are the result of a close collaboration between the AmeriFlux Management Project, ICOS, and CDIAC personnel. This poster will provide an overview of the components of the system and a preview of upcoming functionality.

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 CO₂, water, and energy fluxes across the Americas. The DOE AmeriFlux Management Project (ameriflux.lbl.gov) serves a broad community of flux sites and data users. This poster will present some new resources and highlights, including a new rapid-response flux system that can be loaned to sites with an unanticipated but valuable research opportunity; the long-term AmeriFlux Core Sites; new and ongoing technical QA/QC offerings like calibration gases and site visits; and more.

Early Career Awards

Model-data scaling approaches for assessing the pan-Arctic permafrost carbon feedback

Daniel Hayes (hayesdj@ornl.gov) - ORNL (PI).

The large amount of organic carbon stored in northern high latitude permafrost soils 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. Improving our understanding of permafrost carbon vulnerability and associated climate feedbacks is a major research priority for the scientific community. Here, we describe the development, application and potential uses of a geospatial model-data framework designed to characterize, quantify and scale permafrost carbon vulnerability across the pan-Arctic domain. The framework facilitates the spatial integration and analysis of observational, experimental and model data representing the key system components, namely: 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 carbon dioxide or methane.

The approach works from the “top-down”² perspective designed to provide a much needed first-order, broad-scale assessment of the drivers and responses of the Arctic system carbon cycle using data-driven scaling methods. First, we developed a pan-Arctic regionalization scheme based on a broadly-defined spatial representation of the major environmental controls on the key system components. We then use the resulting Permafrost Regionalization Map (PerM) to organize and analyze the representativeness and variability of a series of data collections quantifying these key system components across the pan-Arctic domain. The results of this synthesis of data collections based on the PerM allows for model benchmarking specific to high latitude processes. We demonstrate this benchmarking approach here by comparisons with the results from a terrestrial biogeochemistry model that we used to simulate the impacts of permafrost thaw on carbon cycling across the pan-Arctic. Finally, we are using this framework to identify key regions of particular vulnerability, 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 Earth System Modeling frameworks.

Methane Oxidation in Boreal Peatlands: A Joint Field, Laboratory and Modeling Investigation

Rebecca Neumann (rbneum@u.washington.edu) - University of Washington (PI).

Natural wetlands currently contribute 20-39% of global methane emissions; but their response to changing climate conditions is unknown because feedback between climate and wetland methane emissions is highly uncertain. Our objective is to improve predictions of methane emissions and constrain climate-methane feedback by focusing on the oxidation side of the methane emission equation. Specifically, we will advance understanding and modeled representations of methane oxidation within the unsaturated zone and soil zone surrounding roots of wetland plants (the rhizosphere). Rhizospheric oxidation, in particular, represents an important sink for methane, capable of oxidizing ~90% of the CH₄ produced in wetlands; however, the process is not well captured by large-scale wetland models where oxidation of CH₄ is usually simply set to a constant percentage of that transported by plants. Our approach involves fieldwork, laboratory experiments, and modeling. We are augmenting fieldwork conducted in Alaskan boreal peatlands that span hydrochemical and permafrost-thawing gradients with controlled laboratory experiments and mechanistic modeling. Results from this effort will inform the development of a dynamic representation of methane oxidation appropriate for large-scale models.

In the first year of the project, we have harnessed porewater data on concentration and isotopic composition of methane and carbon dioxide to determine rates of methane production, methane oxidation and methane loss from a subsurface profile in a boreal bog. Model fits to the data indicate that a large fraction of produced methane was not present in the porewater, suggesting it escaped to the atmosphere. However, the modeled rate at which methane was lost from the porewater far exceeded measured rates of atmospheric methane emission at the site, implying that a majority of the “lost” methane was oxidized once it left the porewater (e.g., in the unsaturated zone or in plant aerenchyma). The results indicate that methane oxidation is a key process at the site, responsible for reducing potential methane emissions by up to 98%.

Ongoing and planned field and lab work build upon these initial results by further quantifying rates of methane production, oxidation and loss within the subsurface, linking these rates to oxygen concentrations measured within the subsurface using optical oxygen sensors, and identifying factors that control subsurface oxygen concentrations. We are concurrently developing a root-scale mechanistic model that we will use to test hypotheses, aid in the quantitative assessment of field and laboratory data, and as a means for discerning the dominant controls over methane oxidation.

Federal Agency-Led Research

Quantifying the interactions between plant water uptake and hydraulic redistribution on the components of evapotranspiration in a mature, unmanaged forest stand

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Evapotranspiration (ET) in unmanaged mature, deciduous, temperate forests has been shown to remain fairly consistent within and among years with varying water availability. Relatively high rates of ET during periods of low soil water availability are largely driven by transpiration from dominant trees. These mature trees have a well-established rooting system with the ability to access deeper reserves of water. When transpiration is halted, typically at night, due to stomatal regulation or low atmospheric demand for water, tree water status can increase to the point where the gradient drawing water from roots to shallow layers of dry soil becomes greater than drawing water into stem and branch tissue. This process of hydraulic redistribution can provide a subsidy of soil water for the dominant trees. However, unmanaged ecosystems are generally composed of several species with, as our results show, considerable overlap between roots of overstory and understory trees, especially in the top 0.5 m of soil. These conditions can result in competition for the 'lifted' water among overstory and understory trees as well as from soil evaporation. Further, some trees maintain water uptake throughout much of the night, either through transpiration or recharge of stem and branch water capacitance. In cases where nighttime water uptake occurs, the canopy becomes a competing sink for lifted water and redistribution to the shallow soil layers may not occur.

To quantify the effect of hydraulic redistribution on tree water use, we deployed above- and below-canopy eddy covariance systems, allowing us to partition the contribution of soil evaporation and shrub and sapling transpiration to the ET budget. We utilized eddy covariance together with sap flux measurements to compare individual species' contribution to total canopy ET. We present data from the first year of this ongoing study, showing that even in years with high growing season precipitation, high evaporative demand in the southeastern U.S. can lead to depletion of both shallow and deeper soil water. Nighttime sap flux (representing movement through tree stems at breast height) often exceeds ET, indicating that this water is resupplying stored stem water used earlier in the day. Furthermore, while the daily amount of transpiration is fairly consistent throughout the growing season, the proportion of water movement at night increases during dry conditions and is greater in diffuse porous than ring porous species.

Climate feedbacks in drylands: linking carbon cycling and energy balance above- and belowground

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Arid and semi-arid ecosystems cover ~40% of Earth's terrestrial surface and make up ~35% of the United States (U.S.), yet we know surprisingly little about how climate change will affect these widespread landscapes. Like many dryland regions, the Colorado Plateau in the southwestern U.S. is predicted to experience climate change as elevated temperatures and alterations to the timing and amount of annual precipitation. We are using a factorial warming and supplemental rainfall experiment on the Colorado Plateau to explore how predicted changes in climate will affect vascular plant and biological soil crust community composition (biocrusts are a surface soil community of mosses, lichens and cyanobacteria that can make up as much as 70% of the living cover in drylands), biogeochemical cycling, and ecosystem energy balance. While some of the responses we have observed to date were expected, many of the results have been surprising. For example, we have seen biocrust community composition shifts in response to altered climate that were significantly faster and more dramatic than considered probable for these soil communities that typically change over decadal and centennial timescales. Further, the biocrust responses to manipulated climate change were notably similar to those commonly observed after physical disturbance. In other words, altered precipitation patterns resulted in effects that were of the same magnitude as driving a 4x4 vehicle over the crusts, a result we were not expecting. In addition, while we continue to observe important climate change effects on carbon cycling - including reduced net photosynthesis in vascular plants and the suggestion of increased CO₂ losses from biocrusts - we have also now found marked treatment effects on the albedo and spectral signatures of our dryland soils. In particular, the changes to biocrust community caused by climate manipulation have significantly affected biocrust albedos: biocrusts in plots receiving +4°C above ambient warming+altered precipitation treatments have albedos >50% greater than control plot crusts. In ecosystems such as these where solar irradiance can reach near potential, these effects could have significant implications for global energy balance. Taken together, the results underscore the fact that: (1) large climate-driven changes to dryland biogeochemical cycling may be the result of both effects on existing communities, as well of relatively rapid shifts in community composition and (2) drylands may provide feedbacks to future climate not only through altered carbon cycling but also via changes to surface albedo.

Institute

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

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Forests recovering from disturbance are strong carbon (C) sinks that play an important role in climate regulation through their influence on the global C cycle. Climate change is likely to alter forest recovery dynamics or even prevent recovery, and changes in disturbance-recovery dynamics will impact the global C cycle. We are using a combination of modeling and data synthesis to understand how and why 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 CO₂ and climate will affect patterns of forest recovery. We are using the Ecosystem Demography model (ED2) to characterize how the physiological and successional mechanisms that regulate the C cycle are altered by elevated CO₂ and climate change. Specifically, we are projecting how forest demography and C cycling will react to elevated CO₂, using data from the Duke Free Air CO₂ Enrichment (FACE) experiment and a nearby chronosequence for model evaluation. The model predicts that elevated CO₂ will alter C cycling directly through ecophysiological effects and indirectly through altered community dynamics (e.g., relative increase in late successional hardwoods). Current work is focused on quantifying and identifying sources of uncertainty in total impacts of elevated CO₂ on forest C cycling, and future plans include examining responses to climate change and modeling forests in other parts of the world. In addition, we are building a database of C cycling dynamics in secondary forests of known age, which is incorporated into the BETY-db database framework for integration with models (including ED2). The database now contains >5,000 records from >150 sites around the world and includes >50 C cycle variables. All elevated CO₂ and warming experiments to date are included. These data are being used to characterize age- and climate-related patterns in C cycling in global forests, to evaluate model runs, and to analyze forest C cycle responses to warming and elevated CO₂.

Solar Induced Fluorescence: Theory and Measurement Approaches

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Measurements of chlorophyll fluorescence have long been a key method for probing the mechanisms of photosynthesis in laboratory studies. Recent advances in satellite spectroscopy have enabled retrieval of chlorophyll fluorescence from terrestrial ecosystems at a global scale. These retrievals show promising potential as an indicator of photosynthetic rate and environmental stress. This poster will explore the mechanistic basis for interpreting and modeling of solar induced chlorophyll fluorescence (SIF) and approaches we are developing to measure SIF at flux towers.

SIF is essentially a leak of photons from photosynthetic membranes, and it is, therefore, related to the flux of photons absorbed by chlorophyll and to biochemical regulation of photon processing in macro molecular complexes associated with photosystem II.

Satellite retrievals of SIF occur at mid-day, conditions where the capacity for CO₂ fixation usually limits the rate of photosynthesis and absorbed light is in excess. While one might expect SIF to be high under this condition the opposite is observed. Regulatory processes open non-photochemical trapping centers that compete with the photochemical reactions at PSII and with the emission of fluorescence under conditions of over excitation. This serves to minimize photo-damage to the reaction centers by this stress.

We have extended a conventional parameterization for photosynthetic biochemistry to simulate SIF in the SCOPE model. The model was then used to evaluate the potential for using retrievals of SIF to estimate GPP, the integrated V_{cmax} of the canopy, the presence of water stress, and biophysical properties such as leaf angle distribution and chlorophyll content.

Obtaining accurate measurement of SIF from field instruments has been challenging because of the very high spectral resolution required. We will describe new instrumentation that we have developed for this purpose. This will be installed at the K34 tower near Manaus and the observations will be compared with GPP and COS flux measured at the site; with simulations using the SCOPE model and with satellite retrievals.

Hydraulic Redistribution of Water through Plant Roots and Implications for Carbon Cycling and Energy Flux at Multiple Scales

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Hydraulic redistribution (HR) of soil water by plants occurs in seasonally dry ecosystems worldwide. During drought, water flows from deep moist soil, through plant roots, into dry (often litter-rich) upper soil layers. Using measurements and modeling, we are exploring small- and large-scale effects of HR on soil water content, microbial activity, and net ecosystem carbon and energy exchange, in seasonally dry ecosystems of the Western U.S.

At the single root scale, we have modeled a 10-cm radial soil domain, with root at center, and simulated solute transport, soil cation exchange, and root exudation and nutrient uptake under two water flow patterns: daytime transpiration without nighttime HR, and daytime transpiration with nighttime HR. During HR, water efflux flushed solutes away from the root, widening depletion zones for key nutrients like nitrate. Outward transport of cations (previously accumulated near the root by transpiration) led to competitive desorption of ammonium from soil further from the root and generation of hotspots of ammonium availability at night. A microbial community and small food web will next be embedded into this dynamic resource landscape to explore how organisms responsible for nutrient and soil carbon cycling respond to these fluctuating resource regimes.

At the ecosystem scale, we have folded Ryel et al.'s (2002) HR formulation into CLM4.5 and examined how well the combined model can simultaneously simulate measured evapotranspiration, the vertical profile of soil moisture, and the amplitude of HR-associated diel changes in water content, at multiple seasonally-dry Ameriflux sites: Wind River Crane (US-Wrc), Southern California Climate Gradient (US-SCs,g,f,w,d,&c), and Santa Rita Mesquite Savanna (US-SRM). In many cases, the combined model reproduced seasonal and diel observations with reasonable accuracy. However, two shrub and one desert sites proved challenging, for as-yet unknown reasons, though at all sites, soil moisture sensors sample from a small fraction of the eddy flux tower footprint, and in at least one site, groundwater in fractured bedrock (not considered in our model) is the source of water for HR. Our next step is to explore how biogeochemistry in soil layers is affected by the inclusion of HR in CLM4.5.

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Large-scale shifts in land metabolic activity indicated by changing seasonal cycle of atmospheric CO₂

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PROJECT OBJECTIVES: This project has the overall goal of producing datasets of atmospheric CO₂ and its isotopes relevant for documenting changes in the global carbon cycle and improving understanding of how land ecosystems may influence and be influenced by future CO₂ and climate changes. It also has a more focused goal of using these and other data to challenge models that depict the response of changing climate and human forcing (e.g. rising CO₂) on northern extra-tropical ecosystems over multi-decadal time scales, using records extended over the past 50 years.

RESULTS: An important result was the study of Graven et al. (Nature, 2013) documenting a large increase in the amplitude of atmospheric concentration seen in airborne and surface data at high northern latitudes from 1960 to 2010. The amplitude trends were found to be of order 50% north of 45°N, but much smaller south of 45N. The amplitude increase evidently requires an increase in summer-time NPP of order 50% focused on boreal forests. Further ongoing work shows that the amplitude at Mauna Loa shows large quasi-decadal variability, which correlates well with the Pacific Decadal Oscillation (PDO) Index, probably in large part owing to changes in water status of western and middle North America that correlate with the PDO. An overall rise at Mauna Loa amplitude of around 15% is not explained, however, by the PDO. The pattern revealed by airborne and ground-based CO₂ data may require both large long-term increases in NPP north of 45°N, and also small reductions in the seasonal CO₂ exchange at lower latitudes.

Additional ongoing work relates to the changing covariation of the seasonal cycles of atmospheric CO₂ and the 13C/12C ratio of CO₂ in the northern extratropics. This data can be used to assess large-scale trends leaf-level intrinsic water use efficiency (iWUE) and changes in ratio of CO₂ partial pressure within leaf (Ci) compared to the free atmosphere (Ca). The conventional wisdom has been that the Ci/Ca ratio would remain approximately constant as CO₂ rises, which would result in no change in discrimination but a modest increase in water-use efficiency. The atmospheric data are generally consistent with a constant Ca-Ci scenario, which increases discrimination, but corresponds to a constant iWUE. The atmospheric data are not easily reconciled with the study Keenan et al. (Nature, 2013) who suggested based on FluxNet data that a large increase in iWUE has occurred in recent decades.

Methane Emissions from Upland Trees

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Background/Question/Methods

Most work on methane 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 methane. There is abundant evidence that upland ecosystems emit small amounts of methane 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 as significant sources of methane in upland forests. Tree’s root systems can extend to soil depths and moistures where abundant anoxic microsites can develop. These sites can produce methane that could enter woody plant tissue. To address these facts we asked the following questions:

1. Do upland trees release methane to the atmosphere?
2. What are the controlling factors that determine the size and timing of upland tree methane fluxes?

We have established two transects across natural moisture gradients in two forests near Annapolis, Maryland. Both tree and soil methane fluxes were measured using chamber methods. Each tree chamber was custom fit to the stem near the base. In addition, porewater methane concentrations were collected at multiple depths near trees. Abiotic parameters such as soil temperature, soil moisture, water potential, and depth-to-groundwater were monitored using a wireless sensor network.

Results/Conclusions

Upland emissions from tree stems were over +200 ug CH₄/m²/hr while the soil uptake was -15 ug CH₄/m²/hr. Methane emissions varied greatly over the year with the highest emissions occurring during the summer months. Factors controlling methane emissions were soil moisture and depth to groundwater. We observed stem emissions and soil uptake in over 13% of our paired stem-soil measurements. This demonstrates that trees can be emitting methane when the adjacent soil is consuming it, challenging the assumption that upland forests are only sinks of methane. Based on our preliminary data, tree mediated CH₄ emissions may be offsetting the soil methane sink of upland forests by 10 to 30%. Future methane budgets and climate models will need to include tree fluxes and the parameters that control methane emissions for accurate accounting and predictions.

Partitioning Autotrophic and Heterotrophic Contributions to Soil Respiration: A Tale of Two Trenches

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Soil respiration (R_t) is an aggregation of two belowground processes, autotrophic (R_a) and heterotrophic (R_h) respiration. R_t is often measured and modeled as a single process, however R_h and R_a typically originate from a variety of species and may respond differently to temperature, soil water content and substrate availability at diel and seasonal time scales

Within the footprint of the EMS tower at Harvard and Howland forest, automated respiration chambers were utilized in conjunction with the trenching method to partition R_t into its components, R_h and R_a . At both sites, in the late fall of 2012, a trench was dug (to 1m depth) around a 5x5m area, severing all roots leading into the treatment plot. Plastic tarp was placed along the walls of the trench and then backfilled. Automated chambers were placed in each of the trenched and un-trenched plots. Fluxes, along with concurrent soil temperature and moisture, were measured at hourly rates from early spring through late fall of 2013. Measurements from the non-trenched plot represent the combined R_h and R_a components, R_t . Fluxes from trenched plot represent, R_h and the difference ($R_t - R_h$) represents R_a .

At both sites, ^{13}C of respired CO_2 was also measured hourly, yielding large numbers of isotopic flux measurements. Although the difference in $^{13}CO_2$ between R_a and R_h sources is small, the large volume of data may allow this approach to yield an independent estimate of their relative contributions.

There is a strong seasonal pattern to the contribution of R_a to R_t at both sites. Peak R_a contributions to R_t occurred in mid-summer when trees were most active. At the Harvard forest R_a peaked at ~30% and at Howland forest, R_a peak contribution to R_t was ~60%. Summing the daily fluxes over the entire sampling season, R_a contributed 23% to the total seasonal estimate of R_t at Harvard and R_a contributed 48% to R_t at the Howland.

Flux data were binned into phenological stages, spring (Apr-May), summer (June, July, Aug to Sept 15) and fall (Sept 16, Oct, Nov). At Harvard and Howland, diel patterns of R_t , R_h differed between trenched and un-trenched plots with the greatest difference occurring during the summer phenological stage.

The contribution of R_a to R_t changed seasonally and at diel time steps depending on the phenological stage, with the greatest influence of R_a on R_t occurring during the summer months, when trees are most active.

Physiological controls of stem respiration and soil respiration in a temperate forest

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Stem respiration from forest ecosystem is an important component of total ecosystem respiration and the forest carbon cycle. Our knowledge in understanding the variation in stem respiration and its governing drivers is limited, partially because empirical measurement of stem respiration is scarce. It has been reported that soil respiration is partially controlled by photosynthesis, but how stem respiration and soil respiration are controlled differently by photosynthesis over the diel scale is unknown.

The objectives of this research are to reveal the diel and seasonal pattern of stem respiration and soil respiration, the connection between stem and soil respiration, and how photosynthesis controls respiration through transport of photosynthate via phloem. The results will significantly improve our ability to model respiration and incorporate the process into earth system modeling.

We developed a novel system to automatically measure stem respiration at a half-hour frequency and to explore the diel pattern and its correlation with soil respiration and root respiration. We hypothesize that the peak value of stem respiration during a day reaches earlier than root respiration, resulting from the transit transport of newly assimilated photosynthate.

We found that the magnitude of stem-area-scaled stem respiration was at the same order as ground-based soil respiration. The diel pattern of stem respiration was primarily driven by temperature variation. But the peak stem respiration during the course of a day was controlled by tree photosynthesis. The peak value of stem respiration during a day reached earlier than root respiration. The CO₂ source of stem respiration was primarily from locally produced stem metabolism, not from xylem water transported from roots.

NGEE-Artic

Development of reduced order models to capture subgrid-scale soil moisture dynamics in a polygonal tundra landscape

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Microtopographic features, such as polygonal ground, are characteristic sources of landscape heterogeneity in the Alaskan Arctic coastal plain. In a future warmer climate, the spatial distribution of soil moisture is expected to be a key environmental factor controlling the rate and products of microbial decomposition of thawed soil organic carbon. Existing land surface models (LSMs) describe physical and biological processes that occur over a wide range of spatial and temporal scales. Methane production and soil moisture dynamics are nonlinearly coupled, thus accurate prediction of mean soil moisture at coarse-resolution alone is insufficient for accurate prediction. Techniques to estimate subgrid soil moisture distribution are required; in this work we present two Reduced Order Model (ROM) methods: (i) A traditional downscaling approach that uses local coarse-resolution solutions to estimate local fine-resolution solution and (ii) a Proper Orthogonal Decomposition (POD) mapping method that reconstructs temporally-resolved fine-resolution solutions based on global coarse-resolution solutions.

We performed multi-year surface-subsurface isothermal flow simulations using the PFLOTRAN model for summer months at six spatial resolutions (0.25 m - 8 m, in increments of a factor of 2). Simulations were performed for four study sites near Barrow, Alaska. Results indicated a non-linear scaling relationship for statistical moments of soil moisture. Coarser resolution simulations were able to accurately capture mean soil moisture for all study sites, but soil moisture variance was significantly under-estimated in coarser resolution simulations. The traditional ROM was able to accurately capture spatial patterns of soil moisture at fine resolution when compared to true fine-resolution simulations (mean error for all study sites was < 1%).

We built the POD-ROMs of the 4-D soil moisture field using simulation results from three summer seasons (1998-2000) for the four study sites individually (single-site) and aggregated (multi-site). The results indicate that the POD-ROM produced a significant computational speedup with very small relative approximation error (< 0.1%) for two validation years not used in training the ROM. We also demonstrated that the POD-ROM approach: (1) efficiently corrects for coarse-resolution model bias and (2) can be used for polygonal tundra sites not included in the training dataset with relatively good accuracy (< 1.5% relative error), thereby allowing for the possibility of applying these ROMs across a much larger landscape. This method has the potential to efficiently increase the resolution of land models for coupled climate simulations, allowing LSMs to be used at spatial scales consistent with mechanistic physical process representation.

Modeling controls on the decomposition of Soil Organic Matter

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Arctic and sub-Arctic soils store vast amounts of carbon, approximately 1700 billion metric tones of frozen organic carbon. This carbon is susceptible to release to the atmosphere due to environmental changes, including those expected under 21st century climate change (e.g., rapidly evolving topography, warming). However, the mechanisms responsible for this susceptibility of soil organic matter (SOM) are not well understood, and uncertainties exist in their representation in Earth System models. To analyze the impacts of these mechanisms on SOM dynamics, we have developed two SOM reaction networks: (1) a relatively simple CENTURY-like network (with labile and recalcitrant pools) and (2) a more complex reaction network (with multiple archetypal polymers and monomers C substrate groups). We test and compare these reaction networks, integrated in the PFLOTRAN and TOUGHREACT models, and their predictions of depth-resolved soil organic matter (SOM). We investigated how the decomposition of SOM depends on various interacting processes (e.g., microbial activity, surface interactions, aggregation, and input C and SOM chemistry). Results indicate that a reasonable combination of sorption parameters, microbial biomass and necromass dynamics, and advective transport can match observations without resorting to an arbitrary depth-dependent decline in SOM turnover rates.

NGEE Arctic: Biogeochemical controls on microbial CO₂ and CH₄ production in polygonal soils from the Barrow Environmental Observatory

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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 CH₄ and CO₂ greenhouse gases released in a potential warming feedback cycle 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 soil organic matter 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 organic and mineral soils of the active layer in low-centered polygons indicate anoxic conditions in most soil horizons. Unamended, anoxic incubations of soils at -2, +4 or +8 °C produced both CH₄ and CO₂, with different response curves. CO₂ formed rapidly while CH₄ production increased slowly after an initial lag, consistent with field measurements previously reported by other groups. This lag correlates with an increase in microbial biomass and the accumulation and consumption of acetate, the primary substrate for methanogenesis. Rates of formation for both CH₄ and CO₂ were substantially higher in microcosms containing active layer O horizon (38-43% total carbon) compared to B horizon (17-18% carbon) samples. Only traces of CH₄ were released from permafrost during incubations, although CO₂ was continually produced by fermentation and anaerobic respiration. The ratio of CO₂ to CH₄ produced decreased with increasing temperature. The temperature threshold for methanogenesis and dynamic time course of CH₄ production indicate that a constant Q₁₀ relationship is not adequate to explain temperature effects from -2 to +8 °C in the low-centered polygons. Physicochemical data from this experiment are available online at DOI:10.5440/1124197.

In contrast to the low-centered polygon incubations representing in situ water-saturated conditions, microcosms unsaturated high-centered polygon samples displayed lower carbon mineralization as either CH₄ or CO₂. In these experiments, the elevated and oxic center samples produced negligible CH₄, while the mineral horizon of subsided, anoxic trough samples released an increasing proportion of CH₄ at 8 °C.

Biogeochemical processes affecting Arctic tundra soil organic matter degradation and greenhouse gas emission

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Organic carbon (C) stored in Arctic permafrost accounts for approximately 25% of the total organic C on Earth that may rapidly degrade with warming climate, releasing greenhouse gases (CH₄, CO₂) to the atmosphere. As part of the Next Generation Ecosystem Experiment (NGEE) Arctic project, we seek to better understand the rates and mechanisms of soil organic matter (SOM) transformation, including the relevant physical, chemical, and biological processes that lead to both C decomposition and/or preservation below ground. We examine spatial and seasonal patterns in aqueous geochemistry and SOM characteristics across an area of tundra landscape in the Arctic to identify factors that increase or decrease rates of organic matter degradation.

Soil and porewater samples were obtained from the Barrow Environmental Observatory (BEO) in northern Alaska. A suite of wet-chemical and spectroscopic analyses including high resolution mass spectrometry (HR-MS), X-ray absorption spectroscopy (XAS), Fourier transform infrared spectroscopy, and high performance liquid chromatography was used to determine (1) CO₂ and CH₄ formation, (2) the abundance of terminal electron acceptors, (3) vertical transport and spatial variability of both organic and inorganic compounds, (4) soil organic C composition and functional groups, and (5) their interactions with soil minerals. We observe a pH gradient from acidic surface water (as low as 4) to near neutral pH in pore-water 20 cm below surface. Dissolved organic C and Fe are dominant ionic species in both surface waters and soil pore fluids. Ferrous Fe(II) increases with depth and positively correlates to dissolved CH₄ in porewater, from which we infer that Fe(III) reduction may serve as a primary metabolism, driving organic respiration in oxygen-depleted areas. Additionally, dissolved concentrations of CH₄, CO₂, and Fe(II)/Fe(III) vary with soil moisture at locations, indicating that geochemistry differences induced by water saturation may determine microbial products of organic matter degradation. HR-MS and XAS analyses of soil and pore water samples indicate highly heterogeneous composition of natural organic matter, with distinct peaks representing aromatic, aliphatic, and carboxylic functional groups and their associations with soil minerals. We discuss potential implications of these findings in understanding sources, rates, and geochemical controls of C fluxes from tundra soils, which form the basis for a computational modeling framework in predicting feedbacks to warming climate.

Representativeness-Based Sampling Network Design and Scaling Strategies for Measurements in Arctic and Tropical Ecosystems

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Resource and logistical constraints limit the frequency and extent of environmental observations, particularly in the Arctic, necessitating the development of a systematic sampling strategy to maximize coverage and objectively represent environmental variability at desired scales. Required is a quantitative methodology for stratifying sampling domains, informing site selection, and determining the representativeness of measurement sites and networks. Multivariate spatiotemporal clustering was applied to down-scaled general circulation model results and data for the State of Alaska at 2 km x 2 km resolution to define multiple sets of bioclimatic ecoregions across two decadal time periods. Maps of ecoregions for the present (2000-2009) and future (2090-2099) were produced, showing how combinations of 37 bioclimatic characteristics are distributed and how they may shift in the future. Representative sampling locations are identified on present and future ecoregion maps. A representativeness metric was developed, and representativeness maps for eight candidate sampling locations were produced. This metric was used to characterize the environmental similarity of each site. This analysis provides model-inspired insights into optimal sampling strategies, offers a framework for up-scaling measurements, and provides a down-scaling approach for integration of models and measurements. These techniques can be applied at different spatial and temporal scales to meet the needs of individual measurement campaigns.

For example, we recently applied this methodology to remotely sensed LiDAR measurements and multi-spectral imagery from the WorldView-2 satellite at a resolution of 2.3 square meters within the Barrow Environmental Observatory (BEO). At this resolution, polygonal ground features—such as centers, edges, rims, and troughs—can be distinguished. Using vegetation distribution data collected at these polygonal ground features, we scaled these measurements to a section of the BEO, where the Next Generation Ecosystem Experiment-Arctic (NGEE Arctic) is making other intensive measurements and performing multi-scale modeling experiments. The resulting map provides distributions of plant functional types (PFTs) that can be used in intermediate- and climate-scale models, as well as providing a basis for up-scaling other measurements. In addition, we are using a similar technique to quantify the representativeness of soil cores and other samples collected within the same area of the BEO to inform future sampling campaigns. Finally, we are applying the representativeness methodology at a coarser spatial resolution to identify poorly sampled regions of global tropical forests. Such areas could be the subject of future intensive observational campaigns because of their importance to the global carbon cycle and their poor representation within current Earth system models.

The NGEE Arctic Data Archive -- Portal for Archiving and Distributing Data and Documentation

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The open sharing of Next-Generation Ecosystem Experiments (NGEE Arctic) data among project researchers, the broader scientific community, and the public is critical to meeting the scientific goals and objectives of the NGEE Arctic project and critical to advancing the mission of the Department of Energy (DOE), Office of Science, Biological and Environmental (BER) Terrestrial Ecosystem Science (TES) program where the strategic intent is to deliver quality scientific data and improved models regarding the potential effects of increasing greenhouse gas concentrations on the Earth's terrestrial biosphere and the role that terrestrial ecosystems play in the global carbon cycle.

The NGEE Arctic project is committed to implementing a rigorous and high-quality data management program. The goal is to implement innovative and cost-effective guidelines, procedures, and tools for collecting, tracking, storing, archiving, and sharing data within the project, the larger scientific community, and the public.

The NGEE Arctic web site is the framework upon which these data management and sharing tools are being implemented. The home page is a resource for project documentation data sharing policies; data management guidance; notification of new data sets available for project and public sharing; and metadata entry tool help files plus provides an email address to contact the Data Team. [<http://ngee-arctic.ornl.gov>]. The Metadata Entry and Data Upload Tool provides the researcher a standardized format to describe field, laboratory, remote sensing, and modeling data products. A feature of the tool allows for the upload of associated data and documentation files for sharing. [<http://ngee-arctic.ornl.gov/ngeemetadata>] Online help is offered in the form of the NGEE Arctic Metadata Entry and Data Upload Tool Tips and the NGEE Arctic Data Management Guidance. During the metadata creation process, it is possible to register your data set to obtain a DOI and create a complete data citation. NGEE metadata records as well as relevant data from other projects are searchable and available for download through the online Data Search and Access Tool available from the NGEE Arctic home page. [<http://ngee-arctic.ornl.gov/data>]. New tools are continually in development to meet the researcher needs of accessing, visualizing, and archiving the NGEE Arctic data products.

Multi-scale modeling of hydrologic and biogeochemical processes in Arctic ecosystems

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Permafrost dominated Arctic soils contains vast stock of frozen organic carbon. As warming climate accelerates the thaw of the permafrost, increasing amounts of organic matter is exposed to respiration leading to the release of carbon into the atmosphere in the form of CO₂ and CH₄.

Terrestrial Arctic ecosystems are sensitive to climate change and disturbance through interactions of complex ecosystem processes and feedbacks. Understanding of hydrologic, thermal, biogeochemical and vegetation dynamics processes is crucial in understanding this sensitive ecosystem. This requires process-level understanding through observations and process-based modeling of the system to simulate the ecosystem behaviour under predicted climate change scenarios.

The Department of Energy's Next Generation Ecosystem Experiments (NGEE-Arctic) project is working to develop process rich representation of Arctic ecosystems in global Earth System Models (ESM). We are developing a multi-scale modeling framework to investigate ecosystem processes at plot to regional to global scale.

Fine scale microtopography in tundra ecosystem exerts important control on local scale hydrology, below ground biogeochemistry and microbial dynamics, vegetation dynamics and surface energy budgets. The multi-scale modeling framework consists of high resolution process based model (PFLOTRAN) that captures these microtopography in three-phase thermal hydrology models for permafrost freeze-thaw dynamics. Parameterized with field based observations the model was successfully applied to understand the control of polygonal ground microtopography (center/ridge/trough) for different landscapes (high-centered/low-centered/transitional polygons). High resolution simulations help constrain the intermediate resolution models which uses geomorphologic features as its building blocks for regional scale simulations.

The reactive transport module developed within PFLOTRAN consists of a complete CLM-CN biogeochemical reaction framework and inorganic N cycle including nitrification, denitrification and transport (leaching). The model also allows for the usage of alternative biogeochemical models (eg. CENTURY), and microbial-enzyme reactions.

High resolution PFLOTRAN has been tightly coupled to Community Land Model (CLM) to improve the representation of hydrology and biogeochemistry in global scale ESMs. Preliminary results from fully coupled thermal-hydrologic-biogeochemical and terrestrial ecosystem processes using CLM-PFLOTRAN are promising to better resolve hydrology, below ground biogeochemistry and vegetation productivity. The multi-scale framework of nested plot to regional to global scale models will also allows for systematic model-data integration of field/laboratory observations.

Pan-arctic ice wedge degradation in continuous permafrost and hydrological implications

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Wetlands underlain by ice wedge polygons occupy a significant portion of Arctic terrestrial landscapes. The different types of ice wedge polygons, i.e. low- and high-centered, with and without well-developed troughs and pits, can cause major differences in the hydrologic cycle that ultimately impacts habitat availability, connectivity and quality of aquatic ecosystems. By using a collection of satellite imagery, ground and aerial photos, we present observations of recent historical ice wedge degradation at multiple locations within the continuous permafrost zones of North America and Eurasia. The subsequent ground subsidence, which is documented at places to have occurred within a 10 yr time period or less, has resulted in major surface water alterations leading to increasing moisture contrasts across the landscape. Informed by the satellite, aerial and in-situ image observations, our hydrologic model experiments explore the impacts of polygon, and specifically trough-type, on watershed-scale water balance components with a focus on the extent and duration of surface water availability and connectivity. The hydrologic model, WaSiM, includes 1D soil heat transfer via conduction and advection linked to the mass balance modules, which include but are not limited to overland flow, ponding, moss and open water evaporation, evapotranspiration, 2D saturated (groundwater) and 1D unsaturated domains. Aimed at simplifying the landscape, the scenarios suggest the importance of trough characteristics in laterally connecting landscape-scale hydrology, controlling heterogeneous distribution of snow and therefore, impacting surface water extent and duration. We propose that not accounting for the ice wedge polygon topography, including ground subsidence or the lack thereof, undermines the effectiveness of any short- (<10 yr) to long-term (>10 yr) projections of local to regional hydrology in the majority of Arctic permafrost lowlands.

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Use of Environmental Tracers for Multi-Scale Investigation of Hydrologic Mixing and Connectivity in the Arctic Coastal Plain, near Barrow, Alaska

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As part of the US DOE, Office of Science, Next Generation Ecosystem Experiment-Arctic project, we have been using environmental tracers (naturally occurring stable isotopes and geochemical species) to understand the hydrology within polygonal ground and the broader landscape in a continuous permafrost area near Barrow, Alaska. Field sampling in late May to early June (2013) during the snowmelt period showed broad hydrologic connectivity of surface water up to the landscape scale. However, the importance of snowmelt water was short lived and by early June, rainfall and the thawing active layer were the dominant sources of water. Broad-scale synoptic sampling in July and September, 2013 revealed a great deal of hydrological heterogeneity between interlake basin areas, drained thaw lake basins, and major drainages. By mid- to late-summer, isotope and chemical data suggest that stagnant or low flow parts of the landscape are common, with little active connection to larger scale drainages. High depth- resolution, passive sampling of active layer saturation in polygonal ground in 2012 and 2013 using diffusion cells often showed well developed and sometimes substantial geochemical gradients for multiple analytes within saturated zones that were less than 50-cm thick. Such gradients imply a lack of vertical mixing within the active zone. Reductions in permeability with depth and lack of strong hydrological gradients likely limit vertical mixing. These results have implications for understanding spatial variability in methane and carbon dioxide production, and surface water evaporation. Hydrological models should reflect the observed rapid loss of snowmelt water, a summer landscape with limited lateral connectivity, and a lack of mixing with depth. Environmental tracers will also be useful for examining the degree and timing of hydrologic connectivity in landscapes with discontinuous permafrost (e.g., Seward Peninsula) or significant topography.

Status of NGEE-Arctic Track 2 Model Development: Incorporating Dynamic Topography in Fine-scale Models

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NGEE-Arctic is developing a process-rich hierarchical modeling framework to better estimate carbon releases from warming Arctic tundra. The scaling framework includes a climate-scale model and intermediate- and fine-scale models. Development of the fine-scale model is proceeding on two tracks characterized by static topography (Track 1) and dynamic topography induced by ice-wedge thawing (Track 2). Computational challenges associated with dynamic topography will be summarized. Dynamic unstructured mesh infrastructure, spatial discretization schemes that maintain accuracy on distorted grid cells, and careful attention to soil energy and water balances in the dynamic meshes have been identified as requirements (Painter et al. 2012). A numerically tractable representation of thaw-induced topographic changes based on calculated melt volumes of subsurface ice will be described. Prototype simulations using the Arctic Terrestrial Simulator (Coon et al. 2012) will also be presented.

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Three-phase models for thermal hydrology of frozen, variably saturated soils

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Models for predicting carbon releases from thawing Arctic soils require reliable representations of soil moisture dynamics in the presence of freeze/thaw cycles and warming trends. Water in soils does not freeze completely at the nominal freezing temperature because capillary forces suppress the energy state of water in small pores, thus allowing some fraction of the water to remain unfrozen. Classical constitutive models that represent that phase partitioning are strictly applicable only to gas-free soils and are thus not adequate for general numerical models that must represent unsaturated conditions. New phase-partitioning models that are applicable to unsaturated conditions will be described. This relationship extends to unsaturated conditions established relationships for gas-free conditions by smoothing a thermodynamically derived relationship to eliminate a jump discontinuity at the freezing temperature. This relationship is shown to compare well with experimental data on unfrozen water content as a function of temperature for different total water content values. The new relationship has been combined with a modified non-isothermal Richards equation and implemented in the highly parallel PFLOTRAN code. The results based on this modified Richards three-phase flow solution are shown to compare well with data from two different column experiments.

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Photosynthesis, Earth System Models and the Arctic

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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 they must accurately represent the huge carbon fluxes associated with the terrestrial carbon cycle. Photosynthetic CO₂ uptake is the largest of these fluxes and is well described by the Farquhar, von Caemmerer and Berry (FvCB) model of photosynthesis. Most ESMs use a derivation of the FvCB model to calculate gross primary productivity (GPP). In ESMs, parameters associated with modeling photosynthesis are usually fixed for a given plant functional type (PFT) and in many cases, fixed for all vegetation. Although Arctic GPP is a small flux relative to global GPP, uncertainty is large. Only four ESMs currently have an explicit Arctic PFT and the data used to derive Arctic specific traits in these models relies on small data sets and unjustified assumptions. Focusing on species representing dominant vegetation and key Arctic PFTs growing on the Barrow Environmental Observatory, Barrow, AK we are investigating key model assumptions and parameterization associated with modeling photosynthesis in the Arctic, and also advancing process knowledge in areas that are not yet represented in models.

The role of lateral transport on storage and fate of soil carbon in permafrost dominated hillslopes and hollows.

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A large fraction of high latitude, permafrost-dominated, landscapes are characterized by hillslopes. In these landscapes, soil carbon both accumulates and is lost through processes that laterally transport carbon. At present, these processes are not included in regional or global landsurface models. We present preliminary model results of a numerical model of soil transport and storage on an idealized cross section of a permafrost dominated hillslope. In this model soil carbon is transported within a thawed layer. The model tracks the erosion of soil carbon along the hillslope and its subsequent storage in an unchannelized hollow at the base of the hillslope. In a simple scenario, where the landscape is blanketed by a carbon-rich layer (such as Yedoma) overlying carbon-poor materials, the progressive transport of material from the hillslopes to hollows results in the net sequestration of carbon in the landscape. This sequestration occurs because carbon-rich soil is transferred from the near-surface layer of the hillslopes into thicker, frozen deposits that accumulate in the hollows. We also investigate potential hillslope transport-driven feedbacks on the storage and distribution of soil carbon by incorporating basic representations of carbon production by an upper vegetation layer and carbon loss through decay within the mobile soil layer. These results are a first step in using models of lateral sediment transport by geomorphic processes to better characterize landscape-scale distributions of carbon. The model results may be used to help guide soil sampling efforts and provides a process-based framework for the interpretation of the sampling data. If confirmed by field data, the model results suggest that the uneven spatial distribution of soil carbon reservoirs in the landscape have significant implications for coupled carbon and landsurface responses to warming. For example, currently unchannelized hollows and valley bottoms are thought to be highly susceptible to erosion and channel expansion in response to climate change driven active layer deepening and increased runoff. If these areas are rapidly incised and eroded, stored carbon will be released and redistributed more rapidly than would be anticipated by thaw processes strictly driven by ground surface warming.

Radiocarbon measurements to assess soil carbon vulnerability in Arctic coastal tundra

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Permafrost soils contain large, old carbon stores, protected from decomposition by frozen, cold, and waterlogged conditions. If climate change causes high latitude soils to warm and dry, carbon emissions from permafrost soils could be an important atmospheric greenhouse gas source. There is no consensus, however, on how high latitude soil carbon decomposition will respond to soil thaw and warming, due to environmental heterogeneity, complex controls on microbial processes, uncertain carbon stocks and flux rates, and poorly understood soil carbon stabilization mechanisms. To address these knowledge gaps, we are using radiocarbon measurements to estimate soil carbon turnover times and temperature sensitivities in polygonal tundra in Barrow, Alaska. Specifically, we ask: (1) how do soil carbon residence times vary with depth across distinct soil features, and (2) what are the relative temperature sensitivities of different age soil carbon pools? Old radiocarbon ages of soil organic matter in perennially frozen soils and deep portions of the seasonally thawed active layer reflect slow historic decomposition rates, and variations in the radiocarbon content of respired CO₂ indicate variable contributions of this old carbon to total decomposition flux. At five times in 2012 and 2013, we sampled soil organic matter and respired CO₂ from low-centered, flat-centered, and high-centered polygons characteristic of a permafrost degradation cycle. We measured the radiocarbon content of CO₂ in surface fluxes and soil pore space from 3 depths in the soil profile, concurrently incubating active layer soils to resolve the ¹⁴C-CO₂ signatures of individual soil layers. Additionally, we incubated soils at 2 temperatures, using radiocarbon measurements of respired CO₂ to determine relative temperature sensitivities of old and recently fixed carbon. Preliminary data show that CO₂ ages increase with depth from modern radiocarbon ages to as old as 3115 BP, and high incubation flux rates indicate availability to microbes. Preliminary results from the temperature manipulation show slight shifts in $\Delta^{14}\text{C-CO}_2$ between temperature treatments, indicating different temperature sensitivities of old and recently fixed carbon. These shifts are particularly pronounced in well-drained, upland soils, suggesting variable stabilization mechanisms across an environmental gradient. This research is part of the Next Generation Ecosystem Experiment (NGEE-Arctic), a multi-institutional collaboration that has the goal of improving models of Arctic greenhouse gas fluxes through combined observational, experimental, and modeling studies. Results from this study will be integrated with a broad range of measurements from the cm- to the landscape-scale spanning biogeochemistry, geophysics, vegetation, microbiology, micrometeorology, and hydrology.

Metagenomics and microbial community profiling across polygon features at the Next Generation Ecosystem Experiment (NGEE)-Arctic Barrow site

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Permafrost soils are one of the world's largest terrestrial carbon storages. With increasing global temperatures, thawing permafrost is altering Arctic landscapes and becoming a potential source of greenhouse gas (GHG) emissions. As part of the DOE's NGEE-Arctic project, we focused to resolve the microbial potential and mechanisms leading to GHG emissions at the Barrow Environmental Observatory (BEO). We collected seasonally thawed active layer soil samples along a transect containing high-, flat- and low-centered polygons for three consecutive years. Additionally, five deep cores -up to 3 m- were taken from flat- and low-centered polygons in the same transect. The microbial community compositions along the active layer (horizontal transect) and in the deep cores (vertical transect) were determined by sequencing of 16SrRNA genes and metagenomes. The sequence data was correlated to in-situ GHG flux measurements, geophysical and geochemical soil characteristics. Differences in elevation, polygon features, soil horizon and moisture content were identified as the main drivers of the microbial community composition differences along the horizontal transect. Especially in flat-centered polygons differences in carbon and nitrogen contents of soil horizons strongly correlated with changes in community composition. Different polygon types shared a large metabolic potential however not all the key metabolic pathways leading to GHG emissions were found across the BEO. For example CH₄ production potential was only found in low-centered polygons and extended to permafrost layers. By contrast, CH₄ oxidation and CO₂ production potential were more prevalent in the high- and flat-centered polygons. Additionally, the metagenome sequence data revealed that capacity for assimilatory nitrate reduction was enriched compared to denitrification and N₂O production. The sequencing approach also revealed dramatic shifts in microbial community composition with depth in the deep cores. While active layers were populated with sequences corresponding to Verrucomicrobia (potential methanotrophs) and Acidobacteria, Actinobacteria were more abundant in the mid- and deeper layers. We further investigated permafrost layers have high salt content; since these layers have a potential to contain liquid water and sustain microbial activity below freezing conditions. 16SrRNA gene sequencing revealed anaerobic CH₄-producing and -oxidizing Archaea as well as chemolithoautotrophic ammonia-oxidizers within the same permafrost layers, suggesting that nutrients in these layers are tightly regulated and recycled. The long-term goal is to use information gleaned from omics datasets to better inform models that will aid in understanding of the biogeochemical cycles in this complex and fragile ecosystem and how they are perturbed by climate change.

NGEE-Arctic: migrating knowledge across scales to improve climate prediction

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Observations, experimentation, and modeling are being conducted across a range of scales in a permafrost tundra ecosystem in an effort to improve process-level understanding of physical, biogeochemical, biological, and ecological dynamics and interactions, with the goal of migrating this new knowledge up in scale to improve climate prediction. Models are being constructed and exercised in a nested hierarchical framework, with very fine-scale process-resolving models being parameterized using multiple observational constraints, and being run over selected sub-regions to inform coarser-scale parameterizations. Observations and laboratory studies in several process domains and across multiple spatial and temporal scales are being used to inform parameterizations, while independent observations and laboratory manipulations are being carried out to evaluate models and quantify model prediction uncertainties. Some of the developments presented here are being targeted for migration to new global-scale climate prediction frameworks. Successful generation of new process-level knowledge and migration of knowledge into predictive modeling frameworks depends on a rapid, accurate, and understandable approach to managing multi-faceted data. The project has developed and is using an integrated approach to collection, sharing, and management of observational, experimental, and modeling data.

Multi-scale Geophysical Studies at the NGEE-Arctic Site

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Improving climate change prediction in high latitude systems requires an accurate understanding of both continuous and threshold-dominated permafrost dynamics. Quantifying the properties and states that govern permafrost dynamics (including variations of ground ice, active layer thickness, soil moisture, soil texture, infiltration pathways, temperature gradients, snow and permafrost distribution, cryopegs) and their impacts on the soil biogeochemistry and geomorphology is challenging because of the coupled nature and wide range of space and time scales over which these processes are manifest. As part of the Next Generation Ecosystem Experiments (NGEE-Arctic), we are developing geophysical-based methods to improve understanding of the complex and dynamic Arctic system across scales. Our studies are underway at the NGEE site in the Arctic Coastal Plain, a region vulnerable to global warming and where significant uncertainties with ecosystem feedbacks to climate exist. Our efforts are fourfold. We are:

(1) Advancing and deploying geophysical methods for improved characterization and monitoring of the Arctic tundra systems. Examples include improved approaches for inverting surface based electromagnetic data and novel multichannel analysis of seismic surface wave for characterizing the permafrost. These studies have revealed the presence of a partially unfrozen saline layer below a shallow permafrost layer which was later confirmed by drilling. Efforts are ongoing to explore if microbial degradation of organic carbon is active in this deeper zone.

(2) Developing stochastic methods to integrate geophysical, remote sensing, and point based measurements to estimate subsurface properties that can be used to initialize or parameterize models or lead to new understanding of system characteristics. Examples include the use of ground penetrating radar and electrical resistivity tomography to estimate active layer thickness, moisture content and snow depth..

(3) Performing dynamic experiments to advance understanding of coupled hydro-biogeochemical processes and associated geophysical signatures. Controlled freeze thaw column experiments are being conducted in the laboratory and include the co-acquisition of geophysical, geochemical and microbiological measurements. Early results are revealing good correlations between geophysical signals and freeze thaw state as well as between surface greenhouse gas fluxes with temperature and thaw depth in the column.

(4) Developing tractable approaches to characterize Arctic systems and the properties that control system functioning across scales. Through jointly using ground- and aerial-based imaging methods, a strong correspondence between land and subsurface property variations has been identified and a zonation approach has been developed to delineate regions having unique distributions of properties that influence microbial carbon degradation and greenhouse gas fluxes.

Characterizing rooting depth distribution and nitrogen acquisition by dominant tundra plant species

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Rooting depth distributions in Arctic tundra are an important factor controlling competition for water and nutrients among plant species. Permafrost thaw and degradation resulting from climate warming may lead to altered thickness of the active soil layer, and a changing vertical distribution of plant-available nutrients. Species with root distributions that provide better access to nutrients in an altered soil profile may gain a competitive advantage. However, our ability to predict how tundra plant communities will respond to such changes is hindered by the fact that little is known about the rooting depth distributions and nutrient acquisition strategies of the dominant plant species.

During July 2013, we conducted an ^{15}N isotope tracer experiment to assess the vertical distribution of nutrient acquisition among three dominant species representing important plant functional types on the Barrow Environmental Observatory in Alaska. We injected a solution of $^{15}\text{NH}_4\text{Cl}$ into the soil in either the organic horizon (3 cm), the mineral horizon (10 cm), or at the permafrost boundary (~ 30 cm), beneath 10 \times 10 cm plots located in homogeneous patches of *Carex aquatilis* (sedge), *Eriophorum angustifolium* (sedge), and *Salix rotundifolia* (deciduous shrub). One week later, soil cores and aboveground plant material were harvested from the plots. Soil cores were sectioned by depth and roots were removed. Soil organic matter and plant tissues were analyzed for ^{15}N content.

An analysis of leaves and stems indicates that both sedge species acquired substantially more ^{15}N from the mineral soil layer than from the organic soil layer, whereas the shrub acquired ^{15}N primarily from the organic soil layer. None of these species acquired much ^{15}N from near the permafrost boundary. The roots of the shrub were located almost exclusively in the organic horizon, which is consistent with the patterns of nutrient acquisition for this species. Contrastingly, the roots of the sedges, though most abundant in organic soil, extended throughout the soil profile, suggesting that root density does not entirely explain the patterns of nutrient acquisition for these species.

Ongoing work includes further analyses of root distributions and of the ^{15}N content of collected roots. Results from this experiment will be used to develop better representations of tundra root dynamics and plant-soil interactions in models. In the future, this experiment could be expanded to include more plant species and plant functional types, more forms of injected nitrogen, or more labeling events in order to assess seasonal variation in nitrogen acquisition.

Scientific Focus Areas (SFA)

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

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Continued TES funding has led to improvements in understanding fossil fuel carbon dioxide 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 fossil fuel carbon dioxide emissions have been completed from January 1950 to December 2010. The basic spatial unit of data is at the scale of nations (which then can be summed to regional and global totals). These data are available in numerical tables or graphically distributed. One of the primary results of this monthly research is that the global monthly time series is statistically significantly different from a uniform distribution throughout the year.

Spatially, the annual and monthly data are gridded at one degree latitude by one degree longitude. This data presentation format has proven so useful to the broader community that others have made several 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 fossil fuel emissions has been concentrated in two areas: global totals and gridded distributions. A new global uncertainty analysis has been completed and submitted for publication in *Tellus*. The analysis includes three separate uncertainty assessments, resulting in a multifaceted examination of the uncertainty associated with fossil fuel carbon dioxide emission estimates. Each assessment has its own strengths and weaknesses and none give a full uncertainty assessment of the emission estimates. This approach grew out of the lack of independent measurements at the spatial and temporal scales of interest. Issues of dependent and independent data are considered as well as the temporal and spatial relationships of the data. The three assessments collectively give a range that spans 1.0 to 13% (2 sigma). Greatly simplifying the assessments gives a global fossil fuel carbon dioxide uncertainty value of 8.4 % (2 sigma). Uncertainty assessments on gridded distributions has begun.

Peer-reviewed publication of this work continues. Since the last TES presentation two years ago, TES funding has contributed to 12 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.

Controls over biogenic volatile organic compounds from Amazon forests as part of GoAmazon

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Emissions of biogenic volatile organic compounds (BVOCs) from Amazon forests affect key atmospheric processes including aerosol and cloud lifecycles, which in turn influence terrestrial physiological processes through changes in precipitation, temperature, and the quality of incoming light for photosynthesis. As a part of the DOE GoAmazon ARM campaign in central Amazon, we are conducting controlled laboratory studies and a multi-year field campaign to investigate the identities, amounts, and biological and environmental controls over tropical BVOC emissions using advanced analytics (TD-GC-MS, PTR-MS, CRDS). In lab studies, connections between BVOC emissions and plant central carbon and energy metabolism is being carried out at the leaf and branch level using dynamic ¹³C-pulse chase experiments. In the field, we are collecting spatial and temporal atmospheric BVOC concentration patterns at the TT34, K14, K34, and ATTO towers and ZF2 canopy walkways. In addition, tree surveys have been initiated to evaluate potential phylogenetic relationships with BVOC emissions. By improving the representation of BVOC emissions within the CESM model with field observations in the Amazon, we will evaluate the impacts of tropical BVOC emissions on aerosol and cloud lifecycles and their associated climate feedbacks to the biosphere.

Full-column Greenhouse Gas Profiles Measured at ARM SGP

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The vertical distributions of CO₂, CH₄, 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 (CO₂, CH₄, 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. In 2012-2013, we 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, while laboratory testing and fluid flow modeling suggest Aircore profiles are likely to resolve the vertical distribution to within better than 1km up to near 30 km. In the coming year we plan to compare Aircore measurements with NASA ground-based and (potentially) OCO₂ satellite remote sensing, and likely develop semi-automated payload recovery. The expected outcome of this project will be an operational capability providing data that supports key DOE science objectives.

Vertical profiles of peat pore water chemistry in a northern peatland reveal dynamic element cycles

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Northern peatlands are globally important, carbon-rich ecosystems, and studies of peatland water chemistry have often been used to identify important biogeochemical processes that regulate nutrient availability and dissolved carbon export. However, patterns in peat pore water chemistry have rarely been examined at a high spatial or temporal resolution. We measured depth profiles (to 3 m) of pore water chemistry weekly from August to November 2013 at 17 locations across an 8.1-ha black spruce-Sphagnum bog at the Marcell Experimental Forest (northern Minnesota). Ten of these locations will be experimental plots for SPRUCE, an ecosystem-scale climate change experiment. The SPRUCE experiment will manipulate temperature and CO₂ concentrations inside replicated, 12-m diameter, open-topped chambers beginning in 2015. These pore water chemistry data characterized the baseline biogeochemical conditions prior to the start of the SPRUCE experiment, and also helped infer how biogeochemical cycles may change in response to warming.

There were striking patterns in the depth profiles of peat pore water chemistry. Pore water in the surface peat was highly acidic (mean pH across plots=3.8), had high total organic carbon (TOC) concentrations (66.3 mg/L), and low nutrient concentrations (ammonium=0.25 mg/L, nitrate=0.005 mg/L, phosphate=0.04 mg/L). Pore water in deeper peat was vastly different, with a pH of 5.5 (a 200+ fold increase in H⁺ concentration), much lower TOC concentrations (28.7 mg/L), and much higher ammonium concentrations (3.43 mg N/L) than in the surface peat. Pore water chemistry also varied spatially across the bog, but the differences across plots were much smaller than the changes in chemistry with depth within any particular plot. The depth profiles from plots in the north end of the bog were distinct from the profiles in the south end, as plots in the north end had higher pH, and TOC and nitrate concentrations. Similarly, depth profiles in plots closer to the edge of the bog (near the transitional zone from the bog to the surrounding upland soils) had higher ammonium concentrations than plots closer to the middle of the bog.

In summary, there were large gradients in pore water chemistry with depth, and smaller variation across the 17 study plots. The low TOC concentrations and high ammonium concentrations in deep peat likely reflect the inherently different chemical and biogeochemical setting of deeper peats. With warming, evapotranspiration is projected to increase and draw down the water table, and deeper peats may become more hydrologically and biogeochemically connected to peatland ecosystem responses.

Lack of explicit representation of mesophyll diffusion explains persistent overestimation of growth rates of historical atmospheric CO₂ by Earth System Models

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In C3 plants, CO₂ concentrations drop considerably along mesophyll diffusion pathways from substomatal cavities to chloroplasts where CO₂ assimilation occurs. Global carbon cycle models have not explicitly represented this internal drawdown and so overestimate CO₂ available for carboxylation, which results in an underestimation of photosynthetic responsiveness to atmospheric CO₂. From 1901 to 2010, the CO₂ fertilization effect (CFE) on global gross primary production (GPP) is underestimated by 0.05 PgC yr⁻¹ppm⁻¹. An explicit consideration of mesophyll diffusion increases the modeled cumulative CFE on global GPP from 915 PgC to 1057 PgC, a 16% correction large enough to explain the persistent overestimation of growth rates of historical atmospheric CO₂ by Earth System Models. Our finding suggests that the contemporary terrestrial biosphere is more CO₂-limited than previously thought.

ORNL's Terrestrial Ecosystem Science Scientific Focus Area -2014

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The TES SFA combines experimental and observational research and process-level modeling in an iterative exchange among (1) hypothesis development from model simulations, (2) the execution of observations and experiments to characterize multi-factor environmental responses of ecosystems and the organisms they contain, and (3) the use of empirical results to parameterize and evaluate ecological models. This continuous research loop allows us to better understand and predict the global terrestrial ecosystem forcing of the earth's climate, and to assess vulnerability of terrestrial ecological systems to projected changes in climate and atmospheric composition. The research is focused on how terrestrial ecosystems affect atmospheric CO₂ and other greenhouse gases and how the ecosystem processes responsible for these effects interact with climate and with anthropogenic forcing factors.

Overarching science questions include: (1) How will interactions among the physical climate, biogeochemical cycles, ecological processes, fossil fuel emissions and land use evolve and influence one another over decades and centuries, (2) How do terrestrial ecosystem processes, interactions and feedbacks control the magnitude and rate of change of greenhouse gases, and (3) How will the magnitude and rate of atmospheric and climatic change alter the structure and function of terrestrial ecosystems and their capacity to provide goods and services to society?

Unique experiments such as the Spruce and Peatland Responses Under Climatic and Environmental Change (SPRUCE) experiment are conducted to quantify biogeochemical responses to environmental and atmospheric change and to improve model-based predictions of the effects of atmospheric and climatic change on ecosystems' function, composition and feedbacks to the atmosphere and climate. SPRUCE will execute a transient belowground warming treatment sequence in 2014 to be followed by whole-ecosystem warming in 2015.

Additional process research and landscape-scale, carbon-cycle observations in understudied ecosystems also serve to provide data for the improvement of mechanistic representations of ecosystem processes within terrestrial carbon (C) cycle and Earth-system models. TES SFA research informs and improves terrestrial land surface and biogeochemistry models, with a particular emphasis on migration of knowledge into the Community Land Model (CLM4) component of the Community Earth System Model (CESM). Integration among experiments, models and observations advances the predictive skill of climate system models through improved fidelity of process representation in their land surface biophysics and biogeochemistry components; and generates and tests new hypotheses which address critical uncertainties in the terrestrial ecosystem components of climate system prediction.

ORNL's TES SFA Data and Model Management and Archiving Facilitate Data Sharing and Model-Data Integration

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Data and Model Management 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 researchers, 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 management systems, repositories, and integration capabilities needed for the collection, storage, processing, sharing, and archiving of data and management of model products.

These capabilities facilitate model-data integration and provide accessibility to model output and benchmark data for analysis, visualization, and synthesis activities.

Active data sharing facilitates delivery of SFA products to sponsors, the scientific community, and the public. Task specific web sites, web-based tools and data center archived products (<http://tes-sfa.ornl.gov/>) enable these interactions.

The Carbon Dioxide Information Analysis Center (CDIAC) at ORNL will be the final destination for many of these archive products (<http://cdiac.ornl.gov>). CDIAC provides long-term system stability, archive longevity, and reliable public data access.

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 CO₂ 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>).

Impact of fire and natural thaw on permafrost microbial ecology

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Arctic soils contain an estimated 12-42% of terrestrial carbon, most of which is sequestered in permafrost. Because of climate warming large regions of permafrost have begun to thaw. Wildfires are also increasing in frequency in the Arctic, thus resulting in additional thaw of permafrost. As a result much of the soil organic matter in permafrost is becoming available for mineralization by soil microorganisms. Understanding the dynamics of carbon release from permafrost requires assessment of microbial functions at different depths. Yet, little is known about the vulnerability of permafrost and the potential response of soil microorganisms with depth to availability of newly accessible carbon sources. Here we aimed to use a combination of molecular “omics” approaches to gain an understanding not only of the microbial composition, but also the functional potential of microbial communities at different depths and the response of permafrost microbes to natural thaw and thaw caused by wildfire. Soil samples were collected from the site of the Boundary Fire at Nome Creek, AK and along a natural thaw gradient at Tanana Valley, AK. At Nome Creek, samples were taken from complete soil profile up to a 1 m depth. At Tanana Valley, triplicate cores were collected across a natural thaw gradient: ranging from permafrost to seasonally thawed active layer to thermokarst bog. DNA, RNA and proteins were extracted from the Tanana Valley samples and DNA from the Nome Creek samples. The DNA was sequenced to provide information about microbial community and functional gene composition (metagenomes). The RNA was sequenced to determine which genes were expressed and which members of the community were more active (metatranscriptomes). Shotgun metaproteomics provided information about proteins produced in the samples and was used to estimate biogeochemical processes. The results from Tanana Valley revealed that some microorganisms were active in permafrost and that Fe reduction could be a survival strategy in frozen mineral soils. After thaw, methanogenesis was the dominant process. At Nome Creek, fire had a pervasive impact on both surface and permafrost microbial community structure and metabolic functions. Especially methanogenesis and denitrification potential was significantly decreased by fire. Together these studies have important implications for the impact of climate change on permafrost and reveal changes in microbial processing of carbon and shifts in biogeochemical cycles that can occur as a result of permafrost thaw.

Climatic and edaphic effects on root- and leaf-litter carbon inputs to temperate forest soils

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The contributions of root- versus leaf-litter sources to soil organic matter (SOM) are not well understood. As part of the Enriched Background Isotope Study (EBIS), our objectives were to study how climate and edaphic factors affect root decomposition, the transfer of root-derived materials to soil, and the transfer of leaf-litter C to mineral-associated SOM pools. We established ¹⁴C-enriched root- and leaf-litter manipulations at four sites representing the climatic extent of Eastern deciduous forest. We measured root decomposition and incorporation of root-derived C into soil for four years. We also assessed inputs of leaf-derived C into the heterogeneous mineral-associated dense fraction (DF) of SOM in site soils by isolating acid-hydrolyzable and acid-resistant C pools from the DF.

Root decomposition progressed through time with an average total mass loss of 27% in Y1, 42% in Y2, 56% in Y3 and 60% in Y4. Root decay constants were significantly affected by climate and edaphic factors. Soils showed ¹⁴C enrichment after only one month, suggesting that root C was quickly transferred to SOM. Across all years, root-derived C retained in soil varied by site and ranged from 13-68% of root inputs. Sites with slower root decomposition rates retained more root-derived C. Soil retention of root-derived C averaged 36% across the studied sites; however, climate and site edaphic factors greatly affected soil C retention. Root-derived C retention was lower at the warmest site than at two of the colder sites, but higher than the cold site with sandy soils. Hence, root litter retention in soils was shown to vary greatly across temperate forests.

Across all sites, 50-75% of the C in the mineral-associated DF was acid-hydrolyzable. The mean turnover time of C in this pool was 1-2 orders of magnitude faster (~35-350 y) than that of the acid-resistant pool (~300-1500 y). After only two years, leaf-derived C accounted for up to 6% of the C in one or both DF pools at some sites, demonstrating that a component with very rapid turnover can exist within both pools. Mid-infrared spectroscopy confirmed hydrolysis removes proteinaceous and lightly decomposed materials (e.g., polysaccharides), which varied among sites. Differences in the SOM chemistries of the two DF pools corresponded well to turnover times. Climatic effects on turnover times were altered by site-specific factors (especially bioturbation and texture).

These results provide new understanding of the factors controlling the movement, fate, and retention of root- and leaf-litter in Eastern deciduous forest soils.

ANL Terrestrial Ecosystem Science SFA: Soil Carbon Response to Environmental Change

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The Argonne TES SFA conducts fundamental research to quantify and characterize carbon stored in soils and evaluate its potential responses to environmental change. SFA research is currently focused on soils of the northern circumpolar permafrost region, where one of Earth's largest carbon reserves is being held in a state of disequilibrium because of the perennially frozen conditions. Global warming is expected to release significant amounts of carbon dioxide and methane from circumpolar permafrost soils to the atmosphere, potentially creating a positive feedback that will accelerate the rate of climatic change. Confidence in model predictions of this mineralization response is limited by knowledge gaps concerning the distribution and potential vulnerability of permafrost-sequestered carbon stocks.

Hence, our SFA aims to quantify the carbon currently preserved in soils of the permafrost region, determine its spatial and vertical distributions, and assess how susceptible this carbon is to decomposition and release to the atmosphere. Interpretation of soil forming processes will be used to iteratively identify under-sampled locations, obtain new data, characterize spatial and vertical heterogeneity, and generate geospatial extrapolations of soil carbon stocks at landscape and regional scales. Empirical tools will be developed to characterize existing forms of organic matter in permafrost-region soils and evaluate their intrinsic potential for mineralization. SFA products will reduce the uncertainties in regional and global simulations produced by coupled carbon-climate models by informing model calibration and by providing observational references for model validation.

Currently, our research is focused on:

1. Characterization of the spatial heterogeneity of soil carbon stocks in polygonal soils. We are studying the distribution of carbon stocks of low-, flat-, and high-centered polygons in the context of the microtopography associated with troughs, rims, and centers. Polygons representing latitudinal and longitudinal gradients across the North Slope of Alaska are being compared to determine if the heterogeneity of soil carbon stocks can be described and generalized by using a super-pedon approach at the scale of individual polygons.
2. Development of mid-infrared (MidIR) spectroscopy as a tool for characterizing the relative degradation state of organic carbon stored in permafrost-region soils. We are building a circumpolar database of MidIR spectra for active layer and permafrost soil horizons. A variety of multivariate statistical techniques will be used to interpret spectra in the context of applicable metadata to enable development of a relative degradation index for mapping the potential vulnerability of permafrost soil carbon stocks.

Drought shifts internal carbon partitioning of recent photosynthates in black spruce trees: From bud to mature shoot

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Springtime bud-break and shoot development induces substantial carbon (C) costs in trees, altering the internal canopy source-sink relationships. Drought stress impedes C translocation delaying shoot development and potentially increasing the total C cost associated with foliar development. We studied effects of drought and re-hydration on shoot development and C use, in 10-year old *Picea mariana* [black spruce] trees to identify and quantify key morphological/physiological processes. Trees were subjected to one of two treatments in a growth chamber; well-watered control (Cont.) or drought and re-hydration (D). We monitored changes in morphological, biochemical (osmolality, [chlorophyll], [nitrogen], [C] and [non-structural carbohydrates (NSC)]) and physiological (rates of respiration (Rd) and light-saturated photosynthesis (Asat)) processes during shoot development. Further, to study functional compartmentalization and use of new assimilates; we ¹³C-pulse labeled shoots at multiple development stages (at individual branch level), and measured isotopic signatures of leaf respiration, NSC pool and structural biomass. Overall shoot development was delayed by drought. Water deficit during shoot expansion resulted in more compact shoots with on average greater (63%) needle osmolality compared to the shoots on the control-trees. The positive non-linear relationship through time between shoot xylem water pressure potential and needle osmolality suggests osmoregulation occurs in all developmental stages. Development of the photosynthetic apparatus was delayed, as shoots on Cont.-trees broke-even (Asat > 0) 14 days prior to D-shoots. Average values of Rd decreased with shoot maturation, ranging from 224.8 to 12.8 and from 96.8 to 12.5 nmol g⁻¹ s⁻¹, in treatment Cont. and D, respectively. ¹²C:¹³C isotopic patterns, indicated that internal C partitioning and use were dependent on foliar developmental stage and treatment. Shoots on Cont.-trees respired a greater proportion of recently fixed C; this was especially true during early stages of shoot development. Mean residence time of C was dependent on rates of respiration more so than C uptake (as Asat). In conclusion, temporary periods of water deficit inhibit C translocation from older organs delaying new shoot development (increasing C input) in black spruce. This entails shifts in internal C partitioning and use to maintain substrate availability for respiration.

Functional unit testing of the Community Land Model at the PiTS-1 field experiment

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Observations of field experiments are often made at the level of the whole-plant, leaves, and fine roots. Classic examples include the photosynthesis response of individual leaves to CO₂ concentration and light, the A-Ci and light response curves, respectively. These and other experimental observations have considerable value for calibrating and testing the fundamental processes of land-surface schemes in earth system models. However, it is generally difficult, if not impossible, to obtain model results for these fundamental processes from the in situ context of fully integrated and coupled land surface and earth system models, particularly under the controlled environmental conditions of field experiments. Thus the productive interplay between model and experiment is hampered. In response, we have developed a framework for extracting individual process representations from the Community Land Model (CLM) of the Community Earth System Model (CESM) into modular units for functional testing. The results of these modules, under the controlled environmental conditions of experimental field measurements, can be generated quickly and compared directly with the experimental observations. Here we report on results for leaf-level observations of loblolly pine (*Pinus taeda*) at the Oak Ridge National Laboratory's Partitioning in Trees and Soils (PiTS-1) field experiment and results from the functional unit module for leaf photosynthesis from CLM parameterized for loblolly pine. Initial comparisons between observations and functional unit results show discrepancies between modeled and observed A-Ci curves, with the model underestimating the magnitude of net photosynthesis, especially at higher temperatures. There is, however, a good match between modeled and observed light response. We then calibrated the model against both observed A-Ci and light response curves using Monte Carlo-Markov Chain (MCMC) parameter optimization. MCMC parameter optimization requires tens of thousands of model runs, numbers made possible by our modular framework and isolation of individual functional units but nearly impossible with even the single-site implementation of CLM. The parameter optimization substantially improves model performance in simulating both A-Ci and light response curves, primarily through increasing the optimum temperature for photosynthesis. These results suggest a focus in subsequent experiments on photosynthetic temperature response at high temperatures and experimental determination of the temperature optimum. Our functional unit testing strengthens and refines the linkage between model and experimental observations as part of the model-experiment (ModEx) concept. The increased modularity of our functional unit testing also provides a platform for structured investigation and quantification of functional uncertainty.

Simulation of the Community Land Model in a pine stand with ^{13}C and shading manipulations

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The Community Land Model is one of the most complicated and best-known Land Surface Models, in terms of its comprehensive parameterization of carbon, water and energy budgets for diverse land types and multiple temporal scales. The CLM has been traditionally evaluated against historical observations from a vast variety of sources, which has caused rapid progresses toward better model versions. Nevertheless, owing to the scarcity and short duration, few attentions have been paid to examine the CLM replication with the manipulative experiments, which are major means to explore the physiological and ecological impacts of artificial controls in environmental variables. The Partitioning in Trees and Soil (PiTS) field observations and manipulations at ORNL were conducted in a pine stand through implementation of adjacent shade treatments and the ^{13}C labeling. It was specially designed to evaluate the modeled carbon partitioning and flux within plants and into soil, and the modeling relationships between these short-term carbon dynamics and the varying environmental drivers. In this study, we target to evaluate the performance of the version 4 of CLM in capturing the carbon and water dynamics observed in this site-level manipulation. Further, to focus on the understanding of modeling uncertainties, we calibrated the default CLM parameters against different stages of the PiTS manipulation by employing the parameter optimization techniques.

Differences in Biomass Distribution and Production Budgets between Cropland and Prairie Grassland

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We study the mechanisms of ecosystem C uptake and retention at two sites with common soil types and climate but differing in management practices. Carbon uptake is measured by the eddy covariance technique. Aboveground and belowground plant biomass, soil microbial biomass, and soil organic carbon (SOC) dynamics are measured via nearby chronosequence on the same soils.

At our study sites (a corn/soybean rotation and a 25-year-old restored prairie near the agricultural site) gross primary production is very similar, averaging about 2500 g C m⁻² y⁻¹. Nevertheless, net ecosystem production (NEP) differs greatly due to the different management practices. The prairie site is a strong and stable carbon sink with an average NEP of -307 g C m⁻² y⁻¹ over 9 years. This NEP sustains net increases in biomass and production of belowground ecosystem components, including SOC stocks and the standing crop of roots and microbial biomass. For the prairie, we have established that, on a yearly basis, about 10-14% of NEP is allocated to SOC accrual, 7% of NEP supports net root production, and 2% of NEP supports net growth increments of microbial biomass. Thus, 23% of the year's NEP sustains net gains of root and microbial biomass as well as SOC accrual rates averaging 43 g C m⁻² y⁻¹. The remaining 77% of NEP is allocated to production of aboveground litter (which is burned as a management practice to maintain the prairie ecosystem and does not contribute significantly to SOC accrual rates).

The cultivated site is rotated annually between corn and soybean, which is a common regional practice. During years when the land is cultivated with corn, NEP averages -270 g C m⁻² y⁻¹. Thus, a proportion of NEP might potentially sustain accrual of SOC and soil microbial production. However, when the field is cultivated with soybean, the land becomes a source of CO₂ (average NEP is 181 g C m⁻² y⁻¹), mostly because the short period of C uptake associated with soybean phenology results in large ecosystem carbon losses. Overall, the positive effects to the production budget that could occur under corn are cancelled by large losses during soybean years, resulting in a lack of energy to sustain SOC accrual under corn/soybean rotations in this area.

Overall, we found that phenological effects on the period of C uptake can be a key factor contributing to sustained ecosystem carbon gains as well as SOC accrual.

Microbial dormancy in terrestrial ecosystem models

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Climate feedbacks from soils can result from environmental change followed by response of plant and microbial communities, and/or associated changes in nutrient cycling. Explicit consideration of microbial life history traits and functions may be necessary to predict climate feedbacks due to changes in the physiology and community composition of microbes and their associated effect on carbon cycling. Existing dormancy models were not theoretically sound and were inappropriate when scaled in ecosystem models. Here, we developed a new Microbial-ENzyme-mediated Decomposition (MEND) model by incorporating microbial dormancy and the ability to track multiple isotopes of carbon. We tested two versions of MEND, i.e., MEND with dormancy and MEND without dormancy, against long-term (270 d) lab incubations of four soils with isotopically-labeled substrates. Although MEND without dormancy fitted well multiple observations (total CO₂ and ¹⁴C respiration, and dissolved organic carbon), this apparently good fit was achieved at the cost of significantly underestimating the total microbial biomass. MEND with dormancy improved estimates of microbial biomass by 20-71% over MEND without dormancy. We observed that the intrinsic microbial carbon use efficiency decreased with increasing temperature by approximately 0.01 per degree Celsius (95% confidence interval: 0.005-0.016 per degree Celsius). Further development of C-N coupled MEND with dormancy illustrated that the C:N ratios in soil organic matter (SOM), dissolved organic matter (DOM) could be well constrained and regulated by microbial stoichiometry. The MEND structure is being tested on the PFLOTRAN-CLM platform to improve representation of CLM subsurface biogeochemistry processes. These efforts should provide essential support to future field- and global-scale simulations and enable more confident predictions of feedbacks between environmental change and carbon cycling.

The effects of whole profile soil warming on decomposition of native soil carbon and ¹³C-labeled root inputs

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Over half of global soil organic carbon (SOC) is stored in subsurface soils (>30 cm). This deep SOC may generate a positive feedback with climate change if warming increases its turnover. However, most warming experiments have only focused on surface soils, where the mechanisms controlling SOC turnover may differ from those at depth. Thus, we have developed two experiments in California, USA to investigate the effects of warming (+4°C) on whole soil profiles. The first warms coniferous forest soils in situ (to 1.3 m), and the second warms grassland soils in field lysimeters (0.5 m deep). In both experiments, we have added highly ¹³C-enriched root substrates to multiple depths 15, 50, and 90 cm in the forest and 10 and 40 cm in the grassland. This labeled substrate will allow us to trace how the transformation of organic inputs (into CO₂ and microbial, particulate, and mineral-associated pools) differs with depth and to measure how native SOC decomposition at different depths is affected by root inputs. Specifically, these experiments will investigate (1) the temperature sensitivity of native SOC and added root substrate decomposition at different depths; (2) the effect of root carbon inputs on native SOC decomposition at different depths; and (3) interactions between warming and root C inputs on native SOC decomposition. We will present our experimental design and preliminary results from the first 4-6 months of warming and its impact on soil microclimate, soil respiration, and soil profile CO₂ concentrations. This study is one of the first to test whole-profile SOC responses to warming and root carbon inputs, and will enhance our understanding of carbon cycling mechanisms throughout the soil profile to improve predictions of soil's role in our changing climate.

Modeling the Hydrological dynamics of the SPRUCE S1 Bog

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Northern peatlands store ~ 30% of the global soil carbon, though only representing ~ 3% of the Earth's land surface. Community Land Model (CLM) component of the Community Earth System Model (CESM) doesn't currently represent vegetated wetlands. To address this limitation, we incorporated key structural and process changes in the CLM. The model with new modifications is informed and tested by SPRUCE experiment. The initial efforts with CLM_SPRUCE have focused on model modifications needed to represent the isolated hydrologic cycle of the bog environment, as well as the characterization of the bog topography into raised hummocks and sunken hollows having distinct hydrologic dynamics and vegetation communities. Our results from the hydrological efforts show that seasonal hydraulic dynamics are reasonable and comparable to the observations. The warming experiments indicate that the responses of hydrological cycle to warming will be significant. These modelling efforts provide a predictive capacity for more realistic seasonal hydrological dynamics to reduce the uncertainties for the northern peat carbon exchange.

Scoping potential microbial responses to warming and drying in the SPRUCE peatland ecosystem.

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The SPRUCE experiment is expected to lead to various changes in ecosystem properties, beyond direct effects of warming that may alter biogeochemical processes mediated by microbial communities. Here we present two lab-scale experiments to scope effects of warming and drying on peat microbial responses.

We examined temperature effects on peat enzyme metrics and how these vary with depth and season. We hypothesized winter and summer communities in near surface peat would show differential enzyme activities and increased temperature response compared to deeper depths where community optima would be narrowly constrained. We measured activity of three enzymes involved in C, N and P cycling using a custom aluminum heat block to obtain highly resolved curves from 2-65°C in ~3°C intervals. Enzyme activity, temperature sensitivity, and C:N enzyme stoichiometry decreased with depth, but showed no seasonal response. Peat N increases with depth whereas C is constant, this is reflected in a concomitant decline in the enzyme C:N mineralization ratio. Proteases were less responsive to temperature ($E_a < 20$) compared to enzymes for C and P depolymerization ($E_a = 20-60$). The stable temperatures in deep peat may result in communities and enzymes specialized for narrow temperature ranges, reflected by a decreased temperature response compared to surface peat that experiences large temperature swings. The small response in protease activity indicates a possibility for decoupling of N, from C and P cycling in the peat with warming.

Warming will likely lower water levels in the SPRUCE chambers, causing strong declines in hummock moisture and moderate declines in hollow moisture. Using laboratory incubations, we compared effects of 75 and 50% of ambient moisture on near surface hollow and hummock peat. We measured enzyme activity, microbial and invertebrate community abundance and composition, microbial biomass, and DOC 2, 13, 42, 91, and 112 days post drying. CO₂ was measured cumulatively. Hummock and hollow peat responded differentially to drying, with hollow communities most affected. Hollow samples at 50% moisture resulted in declines in 6 of 7 enzyme activities within two days that was maintained throughout the experiment. In hollow peat, there was a decline in fungal abundance with drought within 13 days. In hummock samples, two peptidase activities increased with drought, while other enzymes were unaffected. CO₂ respiration was similar among treatments, however 2X more CO₂ was respired from hummock than hollow samples. Overall, hummock microbial communities/processes were largely unaffected by moisture stress, perhaps reflecting the variable moisture levels experienced in native bogs.

LBNL Terrestrial Ecosystem Science SFA: Belowground carbon cycling

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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, we propose 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. We will apply a combination of field and laboratory experiments, microbial ecology, advanced imaging, and numerical simulation modeling in the following tasks: (1) Whole-soil warming experiment: Biogeochemistry; (2) Functional analysis of microbial communities for soil carbon dynamics; (3) Microbial carbon use efficiency: Controls on rates, processes, products; (4) SOM stabilization via organo-mineral interactions; and (5) Soil biogeochemistry and carbon cycle modeling. This research bridges from molecular mechanisms of carbon stabilization to multi-scale biogeochemical models.

Vegetation turnover and nitrogen feedback drive temperate forest carbon sequestration in response to elevated CO₂. A multi-model analysis.

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Predicting forest carbon (C) sequestration requires understanding the processes leading to rates of biomass C accrual (net primary productivity; NPP) and loss (turnover). In temperate forest ecosystems, experiments and models have shown that feedback via progressive nitrogen limitation (PNL) is a key driver of NPP responses to elevated CO₂. In this analysis we show that while still important, PNL may not be as severe a constraint on NPP as indicated by some studies and that the response of turnover to elevated CO₂ could be as important, especially in the near to medium term.

Seven terrestrial ecosystem and biosphere models that couple C and N cycles with varying assumptions and complexity were used to simulate responses over 300 years to a step change in CO₂ to 550 ppmv. Simulations were run for the evergreen needleleaf Duke forest and the deciduous broadleaf Oak Ridge forest FACE experiments.

Whether or not a model simulated PNL under elevated CO₂ depended on model structure and the timescale of observation. Avoiding PNL depended on mechanisms that reduced ecosystem N losses. The two key assumptions that reduced N losses were whether plant N uptake was based on plant N demand and whether ecosystem N losses (volatilisation and leaching) were dependent on the concentration of N in the soil solution.

Assumptions on allocation and turnover resulted in very different responses of turnover to elevated CO₂, which had profound implications for C sequestration. For example, at equilibrium CABLE predicted an increase in vegetation C sequestration despite little increase in NPP, while O-CN predicted much less vegetation C sequestration than would be expected from predicted NPP increases alone. Generally elevated CO₂ favoured a shift in C partitioning towards longer lived wood biomass, which increased vegetation turnover and enhanced C sequestration.

Enhanced wood partitioning was overlaid by increases or decreases in self-thinning depended on whether self-thinning was simply a function of forest structure, or structure and NPP. Self-thinning assumptions altered equilibrium C sequestration and were extremely important for the immediate transient response and near-term prediction of C sequestration.

Microbial dormancy in terrestrial ecosystem models

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Climate feedbacks from soils can result from environmental change followed by response of plant and microbial communities, and/or associated changes in nutrient cycling. Explicit consideration of microbial life history traits and functions may be necessary to predict climate feedbacks due to changes in the physiology and community composition of microbes and their associated effect on carbon cycling. Existing dormancy models were not theoretically sound and were inappropriate when scaled in ecosystem models. Here, we developed a new Microbial-ENzyme-mediated Decomposition (MEND) model by incorporating microbial dormancy and the ability to track multiple isotopes of carbon. We tested two versions of MEND, i.e., MEND with dormancy and MEND without dormancy, against long-term (270 d) lab incubations of four soils with isotopically-labeled substrates. Although MEND without dormancy fitted well multiple observations (total CO₂ and ¹⁴C respiration, and dissolved organic carbon), this apparently good fit was achieved at the cost of significantly underestimating the total microbial biomass. MEND with dormancy improved estimates of microbial biomass by 20-71% over MEND without dormancy. We observed that the intrinsic microbial carbon use efficiency decreased with increasing temperature by approximately 0.01 per degree Celsius (95% confidence interval: 0.005-0.016 per degree Celsius). Further development of C-N coupled MEND with dormancy illustrated that the C:N ratios in soil organic matter (SOM), dissolved organic matter (DOM) could be well constrained and regulated by microbial stoichiometry. The MEND structure is being tested on the PFLOTRAN-CLM platform to improve representation of CLM subsurface biogeochemistry processes. These efforts should provide essential support to future field- and global-scale simulations and enable more confident predictions of feedbacks between environmental change and carbon cycling.

Experiment-inspired Software Design and Ecosystem Modular Testing for CLM Development

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One key factor in the improved understanding of earth system science is the development and improvement of high fidelity earth system models. Along with the deeper understanding of system processes, the complexity of software systems of those modelling systems becomes a barrier for further rapid model improvements and validation. In this paper, we present our software engineering practices for better understanding the Community Land Model (CLM) within an earth system modeling framework. First, we give an overview of the software system of the global offline CLM system. Second, we present our approach to better understand current CLM software structure, data structure computational characteristics using advanced software tools. After that, we focus on experiment-inspired CLM individual ecosystem function testing and new module development, such as preparations for standalone root module development. At last, we layout our plan to further engage broad user communities (modelers, field experimentalists, observation dataset providers, computer scientists, etc.) via web-services and cloud computing. Since better software engineering practices are much needed for general scientific software systems, we hope those considerations can be beneficial to many other modeling research programs involving multiscale system dynamics and legacy scientific software packages.

Plant water relations in an ombrotrophic bog (SPRUCE S1) - partitioning water use and stress tolerance among components

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The 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 to long-term temperature & CO₂ treatments. We have examined baseline plant water relations of plant species at the site to assess seasonal patterns of water use and correlate to carbon uptake through photosynthesis. Sap flow was investigated in shrubs and 5-40 year-old black spruce and larch trees using energy balance or thermal dissipation techniques (TDP). TDP probes were calibrated in situ, by measuring water uptake from cut trees. Water release curves were created for sphagnum mosses, which lack stomata, and related to response thresholds for photosynthesis. Predawn and diel patterns of plant water potential (ψ^*) were also measured seasonally. While the heat balance technique was able to measure sap flow in small diameter stems (e.g., 2-3 mm), early morning thermal gradients and high sap flow conditions both produced artifacts in the data that required filtering and interpolation. Sap flow (per unit sapwood area) was greater in several of the Ericaceous shrubs than in spruce trees. In the trees, sap flow began by late May and was fairly constant over the season until declining in mid-September (larch foliar senescence) and ceasing as temperatures dropped below zero. Midday spruce ψ^* was generally lower than other species, although *Ledum* could also experience low ψ^* (-2.0 MPa). Laboratory measurements of specific leaf conductivity of spruce declined as drought stress increased beyond -1.2 MPa, with the average turgor loss point reached by -2.4 MPa, slightly lower than the turgor loss point of larch (-1.9 MPa). Summer mid-day water potentials in spruce and larch trees approached this turgor loss point. Warming and CO₂ treatments will likely force a change of community composition within this ecosystem due to treatment effects on water availability, and resultant differential water stress among the species. We anticipate being able to capture this response through targeted physiological measurements and more integrated approaches such as chamber-based estimates of system transpiration, changes in soil water content, and through analysis of hydrologic budgets. Insights generated through these studies will be used to improve our understanding of peatland response and resiliency to a changing climate and models of those systems at local to global scales.

Integrating In-situ Data with a Model for Examining Community-level CO₂ and CH₄ flux in a Carbon-rich Peatland in Northern Minnesota

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Peatlands are featured as carbon-rich and vertically dynamic for hydrological and biogeochemical processes, which will significantly influence the ecosystem function and their responses to environmental changes. Therefore, the investigation of community-level flux of carbon dioxide (CO₂) and methane (CH₄), the two most important greenhouse gases, requires a focus on belowground dynamics of hydrological and biogeochemical mechanisms. An ombrotrophic Picea-Sphagnum peatland located on the Marcell Experimental Forest in northern Minnesota is being prepared for experimental manipulations to evaluate carbon cycle responses to warming and elevated CO₂. A custom-designed chamber, which encloses the hummock-hollow topography and allows point-in-time measurements of the shrub, forb, Sphagnum and the complex microbial community, are designed and applied to seasonal measurements of the flux of CO₂ and CH₄ from experimental plots. Periodic observations from August 2011 through July 2013 showed clear seasonal trends with temperature being the obvious driving variable. Interpolation of the observed C flux across annual periods showed dark CO₂ and CH₄ flux to be ~1000 and ~25 gC m⁻²y⁻¹, respectively. After accounting for daytime photosynthetic CO₂ uptake, the net CO₂ efflux from the bog was approximately ~100 gC m⁻²y⁻¹.

These field observational data of CO₂ and CH₄ flux and data of soil and vegetation properties were integrated with a model (improved version of the Community Land Model 4.5) which explicitly represents the carbon processes for CO₂ and CH₄ production and consumption and lateral flow, the critical hydrological processes for wetlands. The modeled seasonality and annual budget of both CO₂ and CH₄ flux and hydrological processes are consistent with field observations. The vertical profiles of concentrations and productions of dissolved organic carbon, CO₂, and CH₄, are examined for their linkages with land-surface fluxes. The reliable performance of the model in simulating hydrological and biogeochemical processes for CO₂ and CH₄ flux suggests that the model is a robust tool for evaluating peatland carbon cycling and its responses to future environmental change. The presented data-model integration approach helps advance our understanding of belowground biogeochemical mechanisms, and would be valuable for supplementing planned manipulative experiments.

The Genetic Potential of Microbial Depolymerization of SPRUCE Peatland in Marcell Experimental Forest, MN

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Amino acid production by microbial extracellular proteases may be the critical step for amine production and release of bioavailable N from forest soil. Yet little is known about the abundance and diversity of the microbial extracellular protease encoding genes in the peatland ecosystems. To evaluate the genetic potential of microbial depolymerization in peatlands, four surface bog and fen peat samples (0-10 cm, two for each) and two deep bog peat samples (25-50 cm and 50-75 cm) were collected from the Spruce and Peatland Responses Under Climatic and Environmental Change (SPRUCE) experiment site, MN. Shotgun metagenomic sequencing was performed on all six samples and guided gene assembly was used to extrapolate microbial extracellular protease genes. We found abundant and diverse proteases within peat metagenomes, comprising nine microbial extracellular protease gene groups and a total of 86,351 microbial extracellular protease genes. These assembled contigs encode for proteases belonging to metallo, aspartic, serine and unknown protease families. The overwhelming majority of genes resembled known proteases of bacterial origin, encompassing 84-95% of the identified proteases per metagenome, while the remaining proteases were similar to protease genes in fungi and archaea. Among identified proteases, aminopeptidase and trypsin encoding sequences were the most prevalent in all samples (approximately 52% and 17% of total assembled microbial extracellular protease genes, respectively). Further, genes similar to extracellular proteases associated with an uncharacterized bacterial protein family were the third most abundant (~16% of total assembled microbial extracellular protease genes). Microbial extracellular protease genes were most abundant and diverse in surface peatland. Approximately 15,025 microbial extracellular protease genes (from 676 species) were assembled from each 0-10 cm sample, compared to ~6,531 (from 286 species) from 25-50 cm and ~4,042 (from 156 species) from 50-75 cm. With increasing depth, the number of observed fungal extracellular protease genes and the number of unique fungal strains that host these genes decreased drastically below 25 cm, while similar phenomenon was observed on bacterial extracellular protease genes below 50 cm. Archaeal extracellular protease genes were more abundant in deep samples than surface samples. Our results indicate that peatland systems have a stratified microbial extracellular protease potential across geographies and depths. High abundance of bacterial extracellular protease genes also suggests that besides fungi, bacteria may play a substantial role in depolymerization of organic matter in peatland systems.

Nutrient regulation of tropical ecosystem responses to environmental changes: a case study in the Amazon region

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In spite of its significance in global carbon(C) cycle, tropical C cycling and the feedbacks from tropical ecosystems to the climate system remain critical uncertainties in the current generation Earth System Models. One of the major uncertainties in the tropics comes from the treatment of carbon-nutrient interactions, especially the lack of consideration of phosphorus (P) cycling and P limitation. We have recently implemented P cycle and C-N-P interactions into the CLM-CN model and the newly developed CLM-CNP model has been evaluated against site measurements in Amazon forests. Here we use the CLM-CNP model to evaluate how P cycling affects tropical C cycle responses to changes in environmental factors such as CO₂ and climate in the Amazon region. Model results show that the introduction of P limitation improved heterogeneity of simulated GPP & NPP across the Amazon region, relative to the original CLM-CN model. NPP simulated by CLM-CNP decreases from west to east across the Amazon basin following the gradient of total soil P, consistent with field observations. P coupling greatly reduces simulated historical CO₂ fertilization effect. Exploratory simulations (2CO₂ and +4°C) show that tropical ecosystem responses to CO₂ increase and warming interact strongly with drought and nutrient dynamics. Our efforts will improve the treatment of carbon-nutrient interactions in the CCSM4/CESM1 carbon cycle and will increase our confidence in predicting future carbon uptake in tropical ecosystems.

Student Abstracts

Seasonality of C allocation to roots in a mid-latitude forest

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Annual forest productivity and carbon storage are affected by the amount and timing of carbon allocated belowground. Many acknowledge the importance of partitioning GPP to above and belowground organs, no study yet has measured belowground C partitioning to root production, respiration and exudation together as it changes over the growing season. Beginning in April 2012 through October 2013, fine root production, respiration, and exudation were measured across the growing season for three stands dominated by common northeastern tree species, *Quercus rubra*, *Tsuga canadensis*, and *Fraxinus americana*, at Harvard Forest in Petersham, MA.

Overall, fine root growth in these stands was characterized by multiple production peaks throughout the growing season that were not explained by soil temperature or indices of precipitation. *Q.rubra* and *F.americana* root growth peaked in early and mid-summer, while *T.canadensis* root growth peaked later in the growing season. Mortality was highest in early spring and during periods of active root growth. Fine root respiration peaked mid-summer for all species. The temperature sensitivity of respiration, estimated using the activation energy, E_a , is lowest in mid-summer and highest in early spring and late fall, reflecting seasonal differences in the apparent temperature sensitivity of respiration. We estimate a growing season C efflux of 310, 389, and 491 gCm⁻²growing season⁻¹, assuming a six month growing season, for *Q.rubra*, *T.canadensis*, and *F.americana* fine roots respectively. Root exudation rate tended to increase over the growing season, summing to 63, 92, and 110 gCm⁻²growing season⁻¹ for *Q.rubra*, *T.canadensis*, and *F.americana*. In all stands, C allocation to roots consumed 35-45% of GPP, with the majority (20-30%) allocated to fine root respiration. The remaining 10-15% is allocated to gross fine root production and exudation. *Q.rubra* allocates relatively more C to gross fine root production than exudation, while *F.americana* allocates C evenly to each process. *T.canadensis* allocates only 3% of GPP to gross fine root production, but this may be due in part to recent infestation by hemlock woolly adelgid. These data demonstrate that root growth is not responsive to broad patterns in temperature and precipitation. In contrast, respiration has a strong relationship with temperature. Other processes, such as exudation, have clear differences between species, but their seasonal pattern is not obvious given inter-annual variability between sample years. Understanding the potential drivers and magnitude of GPP allocated to each process is fundamental to generating predictions about how warming temperatures may affect belowground C balance.

Annual balances of CO₂ and CH₄ from drained agricultural peatlands and restored wetlands in the Sacramento-San Joaquin Delta, California

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Worldwide, drainage of organic soils for agricultural and forestry purposes has resulted in significant soil subsidence, and some of the fastest rates and largest magnitudes of carbon loss attributable to land-use change. The Sacramento-San Joaquin Delta (referred to hereafter as the Delta) in California was drained over a century ago for agriculture and human settlement and has since experienced subsidence rates that are amongst the highest observed in the world. It is well recognized that drained agriculture in the Delta is unsustainable in the long-term, and thus to help reverse subsidence and capture carbon there is a growing interest in converting drained agricultural land-use types to flooded conditions (e.g. restored wetlands and rice agriculture). However, flooding may increase the emission of methane (CH₄) as well as the loss of water via evaporation. I used multiple years of simultaneous eddy covariance measurements at conventional drained agricultural sites (a pasture and a corn field) and flooded land-use types (a rice paddy and two restored wetlands) to assess the impact of drained to flooded land-use change on CO₂, CH₄, and evaporation fluxes in the Delta.

I found that the drained sites were net greenhouse gas (GHG) sources, releasing between 134-350 g-C m⁻² yr⁻¹ as CO₂ and up to 10 g-C m⁻² yr⁻¹ as CH₄. Conversely, the restored wetlands were net sinks of atmospheric CO₂, sequestering up to 450 g-C m⁻² yr⁻¹. However, they were also large sources of CH₄, with emissions ranging from 40 to 57 g-C m⁻² yr⁻¹. In terms of the full annual GHG budget (assuming that 1 g-CH₄ equals 25 g-CO₂ with respect to the greenhouse effect over a time horizon of 100 years), the restored wetlands could be either GHG sources or sinks. Annual net CO₂ exchange at the rice paddy ranged from -283 g-C m⁻² to 95 g-C m⁻² depending on management practices, and the site was always a moderate source of CH₄. The flooded land-use types evaporated 45-200% more water than the pasture or corn sites. Therefore, from a subsidence perspective, restored wetlands and rice appear to provide a benefit for Delta sustainability as they are predominantly large carbon sinks. However, flooding also has secondary effects on the GHG budget through increased CH₄ emissions and higher rates of evaporation.

Investigating the impact of the widespread differential mortality of *Pinus-edulis* in piñon juniper woodlands: informing remote sensing with eddy-covariance.

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Piñon-juniper (PJ) woodlands across the southwestern US are currently experiencing the effects of a pronounced climate change related drought. Recent increases in temperature combined with decreased precipitation and insect pressure is resulting in the selective mortality of *Pinus-edulis* (piñon) in these ecosystems, dramatically altering the physical structure of the system in a patchy and heterogeneous manner. Of specific interest is how events like this will alter ecosystem carbon uptake patterns. Our overall goal is to improve existing mechanistic understanding of how these disturbance regimes and the resulting changes in ecosystem structure affect our ability to predict carbon uptake in PJ woodlands.

We have been continuously monitoring the carbon uptake patterns of a pair of experimental PJ woodlands in central New Mexico using eddy-covariance since 2009. We killed all of the adult piñon in the 4 ha footprint of one of the woodlands and left the other intact as a control. In an effort to scale our measurements to the region and landscape, we have been integrating a wide variety of ground, air, and space borne remote sensing components with the ground-based fluxes.

Our analyses suggest that Landsat scale data are better suited to predicting spatial variability in carbon uptake regimes due to disturbance than more coarse scale sensors, but at 30 x 30 meters the cover specific responses to overstory mortality are undetectable. Our use of high spatial and temporal resolution satellite data from the RapidEye constellation of sensors (5 x 5 meter) has shown that the rapid regrowth of the understory following piñon mortality is pronounced enough to alter seasonal patterns of canopy greenness measured by the used normalized difference vegetation index (NDVI) yet has little effect on gross primary productivity (GPP), potentially overestimating greenness based approaches of remote GPP prediction in disturbed regions. Further, our understanding of these semi-arid systems suggests that a strong decoupling exists between canopy greenness and GPP except during periods of sufficient soil moisture. Specifically, in both healthy and disturbed woodlands regressions between tower measured GPP and ecosystem NDVI were insignificant during periods of seasonal episodic drought. We show how simple models of carbon uptake based on greenness can be improved by including a measure of canopy wetness.

Divergence in how roots and mycorrhizae affect microbial decomposition

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Soil microbes decompose organic matter and this is a critical process affecting fluxes of carbon from soil to atmosphere. To make reliable predictions of carbon fluxes it is imperative we understand drivers of microbial decomposition, but little is known about biotic drivers of decomposition. A prominent hypothesis is that roots facilitate decomposition activity. Plants benefit from facilitating decomposition as microbes increase available nutrients. Plants also host mycorrhizal fungi on their roots, yet few studies have investigated how mycorrhizae affect microbial activity. Mycorrhizae may also facilitate microbial activity, or they may compete with microbes for soil nutrients. In my study, I asked how roots and mycorrhizae affect microbial decomposition activity. Using a soil mesocosm field study, I examined effects of roots and mycorrhizae by progressively excluding them from microbes in soil. I used a ^{13}C substrate to track microbial use of soil carbon into soil respiration. Additionally, I measured activity of enzymes that decompose labile and complex carbon, soil carbon pools, and microbial biomass. I found that roots promoted and mycorrhizae inhibited microbial decomposition of labile carbon. Microbes used the labeled substrate when roots and mycorrhizae were excluded, but used alternative carbon sources, potentially exudates, when roots and mycorrhizae had access. I found no effect of roots and mycorrhizae on microbial decomposition of complex carbon. My data suggest that mycorrhizae use oxidative enzymes to compete with microbes and reduce microbial biomass in soil far from roots, but that facilitation by roots overrides inhibitory effects of mycorrhizae when they are near roots. Overall, my work demonstrates there is spatial variation in microbial decomposition driven by ecological interactions. This becomes important as we use models to scale decomposition up to the ecosystem level.

Understanding effects of roots and mycorrhizae can improve mechanistic models of carbon dynamics. The Microbial Enzymatic Decomposition (MEND) model is calibrated with results from my experiment. The model simulates microbial production of two enzyme pools that decompose two respective carbon substrate pools, which vary in chemical and physical stabilization. Since the model lacks roots and mycorrhizae as mechanisms driving decomposition rates, data from exclusion treatments is used to calibrate the model. We test for importance of roots and mycorrhizae using data from mesocosms with root and mycorrhizal access and compare pool sizes predicted by the model to observed pool sizes in the study. Development of the MEND model with meaningful biological mechanisms represents the forefront of modeling biogeochemical processes.

Variation in Microbial Processes Controlling Carbon Mineralization within 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) time, 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 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 by bulk C content, and that deeper SOM is minimally available for microbial oxidation.

To assess the impact of soil saturation on the chemical composition and bulk abundance of SOM, CO₂ flux and soil moisture contents were monitored at the wetlands. Periods of sub-saturation allow more O₂ diffusion into sediment, stimulating SOM oxidation. Over time, soils exposed to seasonal oxygen incursions accumulate less SOM than permanently flooded soils and sediments. Short pulses of aeration may provide pathways to degrade carbon normally stabilized under sustained anaerobic conditions.

Finally, we are examining fundamental controls on carbon oxidation by examining the role of thermodynamic yield (pairs of electron acceptors and carbon substrates) on the rate and extent of carbon oxidation. Using a combination of respiration measurements and isothermal microcalorimetry, we are quantifying the rate and extent of carbon degradation over a range of microbial energy yields (ΔG). Our results provide a means to determine thermodynamic constraints on SOM oxidation within the complexity of soils/sediments.

TES Lab Research

Pore- to Core-Scale Research to Inform Ecosystem-Scale Soil C Biogeochemistry

Vanessa Bailey (vanessa.bailey@pnnl.gov) - Pacific Northwest National Laboratory (PI), Ben Bond-Lamberty; Chongxuan Liu (Co-PIs).

The spatial separation of soil organic carbon (SOC), microbes, and extracellular activity is an important mechanism of SOC protection in soils and is difficult to represent in predictive models at any scale. Our overarching science objective is to develop the mechanistic understanding of how soil carbon in protected locations is metabolized as a result of pore-scale changes in SOC bioavailability, and to test that understanding for improving the predictive power of ecosystem models. We address this objective by integrating modeling, observations, and experiments. Analyses of global- and ecosystem-scale models are used to identify field sites where pore- to core-scale research can impact model uncertainty by describing SOC metabolism and greenhouse gas (GHG) fluxes. By studying intact soil cores from these sites, we investigate the key species of SOC transported when soil pore connectivity is altered by increasing water content, and the mechanisms by which such protected carbon is mobilized and mineralized. The resulting mechanistic understanding will be used to develop pore-scale reaction networks to describe SOC transformation, and pore- to core-scale reactive transport models to describe SOC distribution and movement affecting net greenhouse gas fluxes. These experimental data and mechanism-based models will be used to test and improve ecosystem-scale models. Such a pore to core to ecosystem-scale analysis and understanding could underpin new mechanistic models of C transformation and transport in soils, improve the predictive power of larger-scale models, and address important Terrestrial Ecosystem Science Program goals.

Multiscale Simulations of Hydrological and Biogeochemical Processes from the Pore to Ecosystem Scales

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A major challenge in hydrological and biogeochemical modeling is the disparity between the spatial and temporal scales at which processes are fundamentally understood and quantified (e.g., pore scales, seconds to days) and the practical applications of these processes in larger-scale modeling (ecosystems to global scales, days to years). In this presentation, we will describe multiscale simulation approaches to bridge this disparity. First, a unified multi-scale model (UMSM) has been developed that uses a single set of mathematical equations to simulate moisture migration and materials fluxes at different scales under both saturated and unsaturated conditions. The UMSM can directly incorporate mechanistic biogeochemical reaction network in soils at the pore-to-core scale. It also allows the pore-to-core scale biogeochemical processes to be seamlessly scaled up to the ecosystem scale through effective parameterization. Coupled to a PNNL-developed reaction-based community land model, the UMSM can be tested against field flux measurements and thus evaluate the transition of reaction rate expressions and parameters from the relatively fine grid scale to coarse grid scale.

Two examples will be provided to demonstrate the capabilities of the UMSM from the pore to ecosystem scales in simulating hydrological processes. Examples include modeling water flow and saturation condition at the pore-to-core scale, and simulating ecosystem-scale hydrological processes at the Disney Wilderness Preserve eddy covariance site. Finally, we describe larger-scale analyses examining how well soil-to-atmosphere C fluxes can be predicted from simple measurements, and test the resulting relationships against both observed and modeled (CMIP5) data.

This research is part of the PNNL/TES project.

Woodland mortality in a long-term drought experiment

Nate McDowell (mcdowell@lanl.gov) - LANL (PI), Sanna Sevanto; Will Pockman (Co-PIs).

We conducted an eight-year drought manipulation in a pinon-pine-juniper woodland in central New Mexico. By the end of the study nearly 80% of the pinon pine and 40% of the juniper trees had died. We observed evidence in support of carbon starvation as a major driver of mortality in both species. Hydraulic failure was also a primary driver though the final causes of mortality were insect-attack. Substantial acclimation of the hydraulic system was observed, resulting in shifts in the ability of species to conduct gas exchange under drought conditions. If drought's continue as predicted, we can expect widespread mortality of both pine and junipers in southwestern USA.

Functioning of wetlands as a source of atmospheric methane: a multi-scale and multi-disciplinary approach at SPRUCE

Jennifer Pett-Ridge (pettridge2@llnl.gov) - Lawrence Livermore National Lab, Karis McFarlane (PI), Xavier Mayali-LLNL; Mike Singleton-LLNL; Ate Visser-LLNL; Brad Esser-LLNL; Tom Guilderson-LLNL (Co-PIs).

To determine how climate change affects processes that determine wetland CH₄ and CO₂ emissions, we are collaborating in a multi-disciplinary study of wetland responses to experimental warming and elevated atmospheric CO₂. Using unique LLNL capabilities and expertise, our goal is a new observational perspective on interacting processes that determine CH₄ fluxes. This work will provide the quantitative process level information required to evaluate the physicochemical parameterizations of wetland CH₄ fluxes and integrate microbial community function into these descriptors. Measurements will occur at the DOE Spruce and Peatland Responses Under Climatic and Environmental Change (SPRUCE) experiment. This site includes warming and elevated CO₂ treatments applied to a boreal peatland forest in northern Minnesota beginning in spring 2014.

Methane (CH₄) is an important greenhouse gas, twenty times more potent than CO₂, but future atmospheric concentrations of CH₄ are uncertain. This is because many climate-sensitive ecosystems release both CH₄ and CO₂ and it is unclear how flux partitioning will occur in the future. Ecosystem observations of CH₄ emissions lack mechanistic links reflecting the processes that govern CH₄ efflux: microbial production, oxidation, and ebullition/diffusional transport. Understanding these processes, and their interactions, is critical to predict biosphere feedbacks to climate change.

Our approach: Our proposed work will identify how key environmental factors change CH₄ fluxes. (1) Link belowground C-sources and processes to atmospheric fluxes of CO₂ and CH₄ through natural abundance isotopic observations of ¹³C and ²H (IRMS) and ¹⁴C (AMS); (2) Identify key microorganisms influencing CH₄ production and consumption using stable isotope probing (¹³C-Chip-SIP, NanoSIMS), (3) Constrain ebullition rates with noble gas depth-profiles of subsurface pore water; (4) Synthesize findings with a biogeochemical box model describing wetland response to warming and eCO₂.

Recent benchtop experiments confirm field study observations that ebullition causes progressive depletion of noble gas concentrations in sediment pore waters. In 2014, we will measure below-ground heating effects on dissolved noble gases at SPRUCE. For SIP analyses, ¹⁶S community data obtained from our collaborators (J. Kostka and H. Lin, Georgia Tech) are being used to design taxon-specific probes for putative methanogens from the Group II Archaea and methanotrophs from the Betaproteobacteria, Gammaproteobacteria, Alphaproteobacteria, Verrucomicrobia, Acidobacteria, and Synergistetes. This work will help parameterize physical and chemical models describing processes from the micro- and molecular scales up to the ecosystem scale and address the need to incorporate microbial community function descriptions into physicochemical models.

Differences in hydraulic strategy show in plant responses to heat and drought treatments

Sanna Sevanto (sanna@lanl.gov) - Los Alamos National Laboratory, Nate McDowell (PI) (project leader); Chonggang Xu (Co-PIs).

Drought-related, continental-scale forest mortality events have been observed with increasing frequency in all forest types during the past 20 years. In the future, droughts are predicted to be accompanied with increasing temperatures that could promote forest mortality via its impact on evaporative demand and plant respiration rates. To tease apart the effects of drought and heat on plant physiology and survival we have built an ecosystem scale manipulation experiment to simulate possible climate change effects in pinon-juniper woodland in Los Alamos NM. Five trees from both species under drought, heat, combined drought and heat, and control treatments are monitored closely until mortality. Drought treatment uses plastic ducts 1.2 m above ground, that direct 50% of precipitation away from the site. Heat treatment is produced with air conditioning units keeping the temperature at 5^oC above ambient all the time. The measurements are targeted to reveal how the trees die based on the current leading hypotheses of plant mortality mechanisms: hydraulic failure and carbon starvation. The monitored variables range from soil moisture content profiles and meteorological data to plant gas exchange, bole and leaf temperatures, and non-structural carbohydrate content of different tissues.

After two years of treatments our results show consistently that heat and drought treatments reduce or slow down plant recovery from the annual summer drought. These effects are more pronounced in junipers than in pinon pine, and could be related to the differences in hydraulic strategies of these plants. Juniper is a very slow growing, desiccation tolerant species that can continue photosynthesizing in much drier conditions than faster growing, desiccation avoiding pinon pine. However, in contrast with common beliefs of these plant types, our results reveal that even if junipers can tolerate loss of leaf water potential much better than pinon pine they actually avoid loss of xylem conductivity more strictly than pinon pine.

University-Led Research

Optimizing ground-penetrating radar for measurement of coarse root biomass and its application in determining elevated CO₂ legacy effects in an 11-year Florida experiment

John Bain (johncbain@gmail.com) - Old Dominion University, Frank P. Day (PI) (project leader) - Old Dominion University; John R. Butnor, USDA Forest Service (Co-PIs).

Coarse roots may play a significant role in belowground carbon sequestration as atmospheric CO₂ levels continue to rise, but temporal and spatial quantification of coarse roots is one of the most difficult aspects of belowground ecology. Ground-penetrating radar (GPR) has been shown to be a useful, nondestructive method of quantifying coarse root biomass. GPR propagates electromagnetic waves into the soil, reflecting a portion of the energy back to the surface when an object is contacted. Despite promising results, this application of GPR is in its infancy, and neither the full potential nor limitations of the technology have been fully evaluated. Using a 1500 MHz antenna, we tested various scanning protocols and thresholds of application for GPR under a variety of environmental conditions in the sandy soils of a sand-hill mixed oak community in Southeastern Virginia. We then applied the optimized protocols to measurement of coarse root biomass in previous experimental plots from an 11-year CO₂ enrichment study at Kennedy Space Center (KSC), Florida that ended in 2007 and in a longleaf pine flatwoods ecosystem at Disney Wilderness Preserve, Florida. Regressions developed for Virginia and Florida showed significant correlations between number of pixels identified as roots by GPR and actual observed biomass ($R^2 = 0.75$ and 0.62 respectively). Multi-directional scans of each sample area were most effective, and the results suggest that all scanning should be completed within a window of consistent weather conditions. We showed that GPR can recognize increasing root density over time, but we were not able to differentiate increases in cross-sectional area. We found that 88% of smaller roots shadowed under larger roots were identified compared with 98% of unshadowed roots. Moisture is a key factor in GPR success as GPR does not identify dead roots after their moisture content has equilibrated with the surrounding soil; only 15% of these roots were identified. Also, even slight increases in soil moisture (5-10%) degrade the root detection capability of GPR. We found that aboveground biomass at the KSC study site was significantly higher ($P < 0.01$) in the previously elevated plots (675 g/m²) compared to the ambient plots (480 g/m²) suggesting there are legacy effects in the form of more rapid aboveground recovery from fire on previously elevated CO₂ plots. Preliminary results also indicate that belowground biomass was higher in the elevated plots as well.

Changes in Soil Microbial Community Structure and Function in a Chronosequence of Warming Experiments at Harvard Forest

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Earth's climate is warming, and this is causing both biophysical (e.g., albedo) and biogeochemical (e.g., carbon cycle) feedbacks to the climate system. Increased temperature seems to alter soil organic matter (SOM) processing, and if warming accelerates SOM decomposition, then carbon (C) stored in soils will transfer to the atmosphere, resulting in a self-reinforcing (positive) feedback to the climate system. Though soil microbes are major drivers of soil C cycling, we lack an understanding of how temperature affects SOM decomposition. In addition, unique decomposer communities can also influence organic matter chemistry, which in turn can affect SOM decomposition. Ongoing field warming sites at the Harvard Forest (Petersham, MA) have experienced 5o C above ambient soil temperatures at three replicated experiments for 5, 8 and 20 years. These experiments now correspond to three distinct phases of CO₂ emissions observed in the oldest field study site. This chronosequence offers a unique opportunity to understand how climate change affects soil microbial community composition and activity over time. DNA was extracted from the warming plots and sequenced by DOE's Joint Genome Institute to test whether the microbial community shifts, under chronically warmed conditions, towards one better suited to access declining stocks of labile C over short-term warming, and to decompose recalcitrant C compounds over long-term warming. Averaged over all samples bacteria comprise 98% of the total DNA. Fungi, in particular, the Ascomycota and Basidiomycota account for 84% of eukaryotic DNA. Only the 20-year warmed site saw a significant change in bacterial community structure in the organic soil horizon, with no significant changes in the mineral horizon.

Multi-scale carbon cycle observations and ecosystem process modeling at Niwot Ridge, Colorado

David Bowling (david.bowling@utah.edu) - University of Utah (PI); Charles Koven, LBNL; Britton Stephens, NCAR; Mark Williams, U. Colorado (Co-PIs).

This project is a multi-scale investigation of carbon cycling at Niwot Ridge, Colorado, and application of the data to improve components of the Community Land Model (CLM). The study involves a paired-site design, including measurements at an alpine tundra location and a nearby subalpine forest (the Niwot Ridge AmeriFlux tower). New observations will extend ongoing continuous long-term CO₂ concentration and CO₂ isotope records to 11 years. We will add new carbon isotope process capability to CLM, and use these datasets to constrain and test the model in site-specific mode. These data will guide improvements to the representation of vegetation and belowground carbon cycling in CLM and provide important tests of modeled terrestrial ecosystem responses to disturbance and climate change.

Results during year 1 include a) successful hiring and training of a postdoctoral physical chemist with expertise in laser spectroscopy (began in Sept. 2013), b) successful hiring of a postdoctoral scientist with expertise in land surface carbon cycle modeling (start date in summer 2014), c) a publication in press in about the isotopic difference between gross primary productivity and respiration fluxes (the ¹³C land disequilibrium), d) initiation of tests of infrared spectroscopic CO₂ isotope instrumentation from all the major commercial manufacturers, e) upgrade of analytical equipment and procedures associated with CO₂ and isotope calibration, and f) continued measurements.

Quantifying the role of topographical and edaphic complexity on coupled energy, water, and carbon cycles in forested, montane ecosystems

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Spatial heterogeneity in the physical structure of the critical zone (CZ) strongly influences both energy and water availability, affecting how water and carbon cycles are coupled in topographically complex terrestrial ecosystems. Predicting how climate change will affect both the structure and the ability of these systems to sequester carbon and provide fresh water requires quantifying how carbon storage has developed under historical climate and a spatially-explicit, mechanistic understanding of how changes in precipitation and temperature will affect these stores in the future. To address this knowledge gap, we utilize spatially explicit observations of landscape structure from Airborne Laser Swath Mapping (ALSM), isotopic and chemical tracers of carbon and water cycling, distributed observations of gaseous and dissolved carbon fluxes, and coupled biogeophysical models in seasonally snow-covered, forested ecosystems across elevation and latitudinal gradients in climate the Rocky Mountains.

ALSM mapping of vegetation at 1m² resolution indicate that spatial patterns in biomass carbon varied strongly with topographic metrics of water availability. Within these landscape-mediated patterns in carbon sequestration driven by microclimate and hydrological redistribution of snowmelt, tree ring basal increment values indicate that growth of major tree species respond positively to both interannual and spatial patterns in water availability and negatively to increased temperature. Foliar $\delta^{13}C$ values further indicate the species response to climate varies with lodgepole pine showing increased water use efficiency in dry year while ponderosa pine does not.

Carbon efflux from these ecosystems was dominated by soil respiration, with relatively small fluvial export in dissolved forms occurring when local water table intersects surficial soils. Instantaneous soil CO₂ fluxes varied significantly across sites and seasons with higher fluxes associated with soil carbon availability, clay content, and shaded slopes. Multiple linear regression analysis across sites and seasons suggests that the response of respiration to a changing will be strongly constrained by spatial and temporal patterns in surface soil moisture.

These results suggest that understanding how catchment ecosystems redistribute water provides powerful insight into the sensitivity and response of carbon cycling to changes in climate. Specifically, decreases in snowmelt-driven recharge may limit topographically driven patterns in plant available water and carbon uptake, while increasing precipitation in the summer is likely to increase surface moisture, promoting respiration and mineralizing stored carbon sources

Towards the development of field methods to characterize environmental controls on rhizosphere priming effects

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We sought to better understand how precipitation and temperature mediate the magnitude and biogeochemical consequences of rhizosphere priming effects, as a first step to improving representations of root-microbe interactions in ecosystem and earth system models. We conducted two field experiments at the Boston-Area Climate Experiment (BACE) - an old-field ecosystem subjected to experimental changes in precipitation (-50% and +50% of ambient precipitation) and warming (from +1°C to +4°C above ambient) since 2008. In experiment one, we quantified how warming and precipitation influence the magnitude and fate of root- and mycorrhizal-derived C inputs. Over a four-month period, root production was greater than hyphal production, although warming had opposite effects on roots (decreased) and hyphae (increased). Greater inputs of root- and mycorrhizal-derived C enhanced microbial activity and accelerated nutrient cycling, especially phosphorus (P) availability. In a second field experiment, we released to soil root exudate mimics of varying chemical quality semi-continuously for four weeks. We found that changes in exudate quality had small but significant effects on microbial processes, often interacting with N availability and temperature-induced changes. Our preliminary results provide some of the first field-based estimates of the extent to which changes in soil moisture and temperature may directly and indirectly alter SOM dynamics via rhizosphere processes, and lay the groundwork for the development of mechanistic models of SOM decomposition under climate change.

Improving Land-Surface Modeling of Evapotranspiration Processes in Tropical Forests

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The humid tropics remain a region of difficulty for land surface models (LSMs). Multiple factors contribute to this problem. In moist tropical regions high humidity, leaf wetness, and cloud cover can combine to suppress forest water use below the potential amount indicated by larger-scale models. Mountainous tropical areas pose additional difficulties, as standard modeling and measurement techniques are not readily applied in rough terrain. In a recently-inaugurated project, a combined program of field measurements and regional-scale modeling of the mountainous tropical rain forest of Costa Rica has been undertaken to provide improved methods of handling these regions in LSMs. Specifically, the project will: 1) collect in-canopy and above-canopy hydrometeorological measurements at the Texas A&M Soltis Center in Costa Rica; 2) develop a new conceptual framework for modeling wet canopy processes based on this new dataset; and 3) appropriately revise the Community Land Model to improve its estimates of evapotranspiration in/from tropical forests. Initial work has included partial installation of instrumentation on a 130 ft tower in the canopy, and development of a system for real-time transmission of the collected data over the internet.

Large variability in ecosystem models explains a critical parameter for quantifying GPP with carbonyl sulfide

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Understanding gross primary production (GPP) at regional and global scales is challenging with existing methods but critically important for exploring carbon-climate feedbacks. An emerging technique for quantifying large-scale GPP is based on the relationship between atmospheric carbonyl sulfide (COS) and GPP. The COS tracer approach hinges on a robust understanding of the relative uptake of COS to CO₂ by plants. While ground-based studies using plant chambers and eddy flux platforms finds a narrow range of possible values for relative uptake, results from atmospheric modeling studies are inconsistent. Here we study this discrepancy by exploring the underlying data from previous atmospheric modeling studies and conducting new regional modeling simulations over North America. We find that the inconsistency in previous atmospheric modeling studies can be explained by the variability in ecosystem model estimates of GPP. Furthermore we find that the uncertainty in relative uptake is much smaller than the uncertainty in GPP which suggests that the COS tracer approach could be useful for constraining GPP at regional and global spatial scales.

Incorporating below ground biology and soil physical properties into a soil carbon degradation model through experimenting across ecotypes

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Belowground processes are critical in understanding carbon (C) cycling, yet our understanding and modeling of the soil physical and biological processes that regulate soil organic matter (SOM) turnover are largely empirical and contribute to reduced confidence in terrestrial C balance under global change. Soil properties and biological communities contribute to C loss and gain, which vary significantly by ecosystem and soil type, but current C cycling models fail to incorporate these interacting factors. For example, mycorrhizal fungi are an integral link to carbon cycles in ecosystems because they exchange SOM-derived nutrients for plant-assimilated C, yet their activity, and how their regulation of carbon dynamic might change by soil type, is often not considered in models. The failure to consider the role of the integrated biological community - microbes, mycorrhizal fungi, and plant roots - on soil C turnover may render models incapable of predicting responses to environmental change. Our project will fill this knowledge gap by modeling and experimentally manipulating the biological community in situ across diverse ecosystems, thus increasing our ability to predict and model the extent to which soils in terrestrial ecosystems will be an atmospheric net C source or sink.

Our work has three aims: (1) to examine degradation of different soil organic C (SOC) substrates in situ in diverse ecoregions that are underrepresented in global carbon models, (2) to manipulate soil biological community access to SOC, and (3) validate the Microbial-ENzyme-mediated Decomposition (MEND) soil C model using field data. To achieve these aims, we will establish experiments that manipulate substrate complexity (starch and lignin) and biotic activity (roots and mycorrhizal fungi) in three distinct ecoregions (tropical lowland forest, peatland, temperate forest) that harbor three distinct, but common soil types. Since our prior work showed that soil types have different abilities to sorb substrates with differing complexities, we will examine breakdown of starch (intermediate complexity) and litter (high complexity). The rate of flux of these three substrates between SOC, dissolved organic C, and microbial biomass C depends on soil sorption properties and microbial enzyme activity in the MEND model. While the model uses parameters from microbial systems, we expect the presence of roots and rhizosphere organisms to contribute to soil C degradation indirectly through enzyme production and exudation (priming). Thus, we will manipulate root and fungal presence to determine if separate parameter sets stemming from each rhizosphere functional group is a necessary component of the model.

Confronting models with regional CO₂ observations to improve interpretation of drought stress and emissions (anthropogenic and fire)

James Ehleringer (jim.ehleringer@utah.edu) - University of Utah (PI), John Lin, Utah; Britt Stephens, NCAR; Peter Thornton, ORNL; Robert Andres, ORNL; (Co-PIs).

This project focuses on the consequences of drought and emissions (fire and urban) for atmospheric trace gas concentration and stable isotope composition (carbon dioxide, carbon monoxide, methane). We expand on a well accepted atmospheric model (STILT-WRF) as a tool to evaluate stable isotope fluxes in CLM/CESM-related models through existing, long-term data sets from six long-term observatories as well as from field campaigns where high-precision trace gas concentration and isotope measurements can be made along the 750-km transect from western Utah through central Colorado.

Spatial Variation in Microbial Processes Controlling Carbon Mineralization within Soils and Sediments

Scott Fendorf (fendorf@stanford.edu) - Stanford University (PI), Marco Keiluweit, Stanford University; Michael Schaefer, Stanford University; Chris Francis, Stanford University; Markus Kleber, Oregon State University; Thomas Wanzek, Oregon State University; Peter Nico, Lawrence Berkeley National Laboratory; (Co-PIs).

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 metabolism 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 manipulations of field samples and in-field measurements to examine if soil structure and carbon availability interact to impose respiratory constraints on organic matter mineralization rates and thus storage.

We have developed a novel diffusion reactor coupled with an optical imaging system that allows visualizing spatial and temporal redox dynamics at the soil aggregate-scale. Combining these in-situ measurements with analysis of carbon chemistry, electron acceptor profiles and reactive transport modeling, we are determining the micro-scale distribution of operative microbial metabolisms and their cumulative impact on SOM mineralization rates. Our field studies comprise two sites: an upland temperate site that takes advantage of a series of soils with systematic variations in soil texture and structure, and a second site within an active tropical floodplain situated within one of the mega-deltas of Asia. Within the upland site, we are testing whether oxygen availability and redox state are good predictors of total carbon contents and chemistry across pedon-, horizon- and aggregate-scales. Within the tropic delta, we are comparing the abundance and chemical state of SOM at three locations having varying degrees of saturation (uncultivated seasonal wetlands, cultivated wetlands, and permanent lakes) by measuring total carbon content and chemistry, the latter deduced principally with C (1s) near-edge x-ray absorption fine structure (NEXAFS) spectroscopy. Collectively, our results quantitatively place the importance of aggregate-based heterogeneity in microbial redox processes on the rate of carbon mineralization.

Nutrient Cycle Impacts on Forest Ecosystem Carbon Cycling

Joshua Fisher (joshbfisher@gmail.com) - UCLA (PI), Richard Phillips, Tom Evans (Indiana University) (Co-PIs).

The goal of our project is to develop a predictive framework for improving and integrating plant-soil carbon (C) and nutrient dynamics into Earth system models through a combination of recent advancements in plant nutrients modeling and measurement techniques. We have thus far found 5 main results:

First, we discovered two types of ecosystem nutrient economies governed primarily by the type of dominant mycorrhizal association - arbuscular mycorrhizae (AM) or ectomycorrhizal (ECM). AM-dominated forests result in inorganic nutrient economies, whereas ECM-dominated forests result in organic nutrient economies.

Second, drought resiliency is significantly different between AM- and ECM-dominated forests. During the middle of our project in 2012, one of the worst droughts to hit the US Midwest was centered on our long-term study site (i.e., AmeriFlux site Morgan-Monroe State Forest, Indiana). We leveraged our on-going measurements to show that the increased water stress outweighed the benefits of the longer growing season on C storage.

Third, we conducted a girdling manipulation experiment, and found that severing belowground C allocation led to strong and persistent declines in rhizosphere C and N mobilization of ECM-dominated forests, but not AM-dominated forests. This supports the understanding of a strong coupling between belowground C allocation in ECM soils with the mobilization of limiting nutrients.

Fourth, we included the C costs of nutrient acquisition from mycorrhizae into the C economics optimization framework of the Fixation & Uptake of Nitrogen (FUN) model, and found that the performance of FUN significantly improved against in situ measurements. We coupled FUN into three larger land surface models - CLM, JULES, and Noah-MP.

Fifth, we were able to detect mycorrhizal association from satellite remote sensing across large scales, explaining 81% of the variance from 66,000 trees within mixed-mycorrhizal forests. This approach represents a significant paradigm shift in understanding how mycorrhizal association influences canopy spectral signatures, and will enable improved prediction of nutrient cycling across large scales.

Climate change alters woody shrub carbon storage and utilization in a moist acidic tundra

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Permafrost warming in the climate sensitive Arctic tundra has been linked to shifts in vegetation, from tussock dominated to tussock/shrub systems. This vegetation shift has the potential to not only impact the abiotic conditions, but also the energy balance and biogeochemical cycling of these systems; as plant assimilation, respiration, C allocation, and rooting depth may differ between plant functional groups. In order to better understand woody shrub responses to these changing conditions, we assessed leaf-level morphological and gas-exchange parameters of dwarf birch and diamond-leaf willow in conjunction with site level abiotic parameters across a simulated winter (snow fence) and summer (open-top chamber) warming experiment at a moist acidic tundra at the Toolik Field Station in Alaska. Additionally, we incubated ephemeral organs (fine root and leaf) while concomitantly analyzing bulk tissue (fine root, coarse root, stem and leaf) for ^{14}C to assess the ages of metabolic and structural carbon. Our results indicate a positive correlation between summer soil thaw depth and leaf surface area indicating hydrological responses of both species. Additionally, leaf area was higher in the summer warming treatment relative to non-summer warming treatment in both the snow addition and the control treatments. Furthermore, we found that diamond-leaf willow exhibits elevated assimilation rates relative to dwarf birch, a pattern maintained when light response curves were constructed at elevated CO_2 (800 ppm). We observed species-specific metabolic (respired $^{14}\text{C}\text{-CO}_2$) and structural (bulk ^{14}C) responses to both summer and winter warming. Both shrubs were more metabolically active (younger respired CO_2 age) in the winter warmed treatment relative to control. In diamond-leaf willow, perennial coarse root tissue exhibited a differential response to warming (older in the summer warmed treatment while younger in winter warmed treatment). While in dwarf birch, perennial tissues are younger in winter warmed and summer warmed areas relative to their respective controls. These responses highlight the forcing imposed by woody vegetation in arctic regions with the potential to increase net primary production in addition to positive feedbacks on winter snow depth, soil temperature, and moisture.

Effects of Regional Groundwater on Tropical Rainforest Streams: Carbon Degassing and Particulate Organic Matter.

David Genereux (genereux@ncsu.edu) - North Carolina State University (PI), Dr. Christopher L. Osburn, North Carolina State University; Dr. Steven F. Oberbauer, Florida International University; Dr. Diana Oviedo-Vargas, North Carolina State University (Co-PIs).

Ecosystem carbon (C) budgets are fundamental for understanding global C cycling, including the role that connections to deep Earth C reservoirs play in C budgets. Our study addresses these topics by examining how inputs of deep regional groundwater affect C budgets and fluxes in a tropical rainforest. Our research has focused on two adjacent watersheds at La Selva Biological Station in Costa Rica, the Arboleda and Taconazo. Both streams are similar in most aspects except that the Arboleda stream receives a significant contribution of old (~3000 years) regional groundwater (~34% of the total discharge), and the Taconazo does not. Recent results focus on two surface water pools/fluxes: particulate organic matter (POM) and C degassing.

Routine sampling of POM during 2012-2013 showed that particulate organic C (POC) was somewhat lower in the Arboleda (0.6 ± 0.3 mg/L) than in the Taconazo (1.0 ± 0.5 mg/L), likely as a result of the Arboleda being diluted by regional groundwater. Also, we found differences in C stable isotope abundance (Arboleda $\delta^{13}\text{C-POC}$: $-23 \pm 8\text{‰}$; Taconazo $\delta^{13}\text{C-POC}$: $-30 \pm 4\text{‰}$) and C:N ratios (Arboleda: 22 ± 13 ; Taconazo: 15 ± 2) between streams. We hypothesize that these differences may be due to the regional groundwater inflow at the Arboleda, or a larger contribution of C₄ plants to the POC pool from swamps in the Arboleda watershed, two hypotheses to be addressed with other observations. Through high-frequency sampling of storms events, we found that the differences in POM between streams became diminished at high-flow conditions, suggesting a shift in POM sources during high discharge events toward C₃ vegetation and soils. POC fluxes from the Arboleda watershed seem to be partially regulated by the connection to regional groundwater and local hydrologic conditions.

Early 2014 data indicate that regional groundwater inputs to the Arboleda cause a major increase (~4x) in stream water dissolved CO₂ concentrations. As a result, CO₂ degassing fluxes across the stream-air interface in the Arboleda were ~4x larger than those in the Taconazo. In contrast, stream methane (CH₄) concentrations in the Arboleda and Taconazo were similar (1.9 ± 0.3 and 1.3 ± 0.1 μM , respectively), as were CH₄ degassing fluxes normalized by watershed area (0.123 and 0.097 g C/m²y, respectively). Connections to deep C-rich groundwater are a common feature in many regions around the world, and results from our research highlight that these links have the potential to influence watershed-based C budgets.

Carbon and water cycling following low-severity disturbance in an Upper Great Lakes forest: Empirical and modeling results from an AmeriFlux core site

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Disturbance modifies forest physical structure and composition, which may in turn alter biogeochemical processes central to carbon (C) and water cycling. In the Upper Great Lakes region, disturbances are transitioning away from severe events that cause forest stand replacement, and toward lower-intensity disturbances that result in partial canopy defoliation or loss of selected species. These low-severity disturbances include partial harvests, wind, pathogenic insects, diseases, and age-related senescence. The response and mechanisms supporting the recovery of C and water cycles following low-intensity disturbance are poorly characterized, with most prior empirical and modeling studies examining the biogeochemical implications of severe stand-replacing disturbance.

At the University of Michigan Biological Station AmeriFlux core site, we are using long-term records of C and water cycling from unmanipulated control (US-UMB) and experimentally disturbed (US-UMd) forests to quantify disturbance-related changes in biogeochemical cycling and identify the underlying mechanisms supporting their resilience to disturbance. The Forest Accelerated Succession Experiment (FASET), in which >6,700 canopy dominant *Populus* (aspen) and *Betula* (birch) trees were stem girdled within a 39 ha area, employs C and water cycling measurements within paired US-UMB and US-UMd meteorological flux tower footprints.

The C cycle at our site has exhibited striking resilience to low-intensity disturbance, with sustained net ecosystem production (NEP) following the senescence of a third of canopy trees. Disturbance-related changes in canopy physical structure are associated with improved resource-use efficiency, providing a mechanism for sustained NEP as trees die. We found that the water cycle responded to low-severity disturbance through modified transpiration. Transpiration per tree and per sap-wood area increased following disturbance, with responses varying among hydrological functional types. Maples (a diffuse porous species) exhibited greater water stress and a decrease in transpiration because hydraulic stress increased following disturbance.

We find that ecosystem models poorly simulate biogeochemical responses to low-severity disturbance. In partnership with the DOE Pacific Northwest National Laboratory, we examined whether big-leaf (Biome-BGC) and gap (ED and Zelig) models accurately simulate NEP observed in our experimentally disturbed US-UMd site. Both ED and Zelig gap models substantially over-estimated the response of NEP to low-severity disturbance, predicting large declines in C uptake. The big-leaf Biome-BGC model more accurately simulated NEP following disturbance, but its mechanistic basis for resilience was not in agreement with observation. These results have implications for biogeochemical modeling at the global scale; both Biome-BGC and ED are part of the development stream of NCAR's Community Land Model and DOE's forthcoming ACME.

Carbon Dynamics of the Greater Everglades Watershed and Implications of Climate Change

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Peatlands (wetlands with thick soil organic layers) are common globally, containing more than 30% of the terrestrial carbon (C) pool. While most research has focused on more expansive high latitude peatlands, subtropical and tropical peatlands have comparable depths of soil C (often >10m) and are at equal if not greater risk of degradation and soil carbon loss due to altered climate and disturbance regimes as well as land use change. The Florida Everglades are an example of a low latitude wetland watershed with extensive peatland carbon stocks subjected to a myriad of environmental pressures due to climate change and anthropogenic forces that place these C stocks at risk. Within the headwaters region of the Everglades watershed, we are quantifying ecosystem C cycling along a hydrologic gradient ranging from xeric pine flat wood forests to inundated sawgrass peatlands using an array of methodological approaches. Eddy covariance measurements of CO₂ and H₂O were collected at all sites, with added at the depression marsh and sawgrass peatland sites. Preliminary results from 2013 indicate that all sites are acting as a sink for CO₂, although the sites are distinct in their seasonal source/sink dynamics. The sawgrass peatland is the largest CO₂ sink while the depression marsh is the smallest. The two wetlands are both sources of CH₄, though the sawgrass peatland has produced only 60% of that of the depression marsh, despite having a longer hydroperiod. Additionally, a series of closed chambers have been installed at each site to quantify community-scale C exchange and develop response functions with environmental drivers. Open-top chambers will be installed on a subset of these chambers to examine the effects of passive heating on C flux. Ground Penetrating Radar (GPR) surveys are being used to estimate peat thickness at high spatial resolution and belowground root biomass. Aboveground biomass has been collected seasonally in plots across all the study sites. Initial development has been completed to represent the mixed pine/depression marsh landscape within the Community Landscape Model (CLM). Using the stock quantifications and flux response functions developed through this study, we will further parameterize our model framework to better incorporate low-latitude wetland watersheds in CLM and Earth System Models.

Spatial patterns and source attribution of CH₄ emissions in an urban airshed to regional/global methane budgets

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Urban areas are increasingly recognized as a globally important source of methane to the atmosphere; however, the methane budget of urban sources is not yet well constrained in global models. Recent atmospheric measurements in Los Angeles, California, USA, suggest that more than one third of the city's methane emissions are unaccounted for in bottom-up inventories. We collected on-road atmospheric measurements of methane and a suite of complementary trace gases across the Los Angeles Basin during June 2013 to quantify fine-scale structure of methane variability within the Basin. We targeted known methane emitters and representative land cover across the Basin as reference points.

Roughly half of local methane enhancement over the study area was associated with concentrated hotspots of atmospheric methane, with the remainder present in well-mixed urban air. Non-hotspot measurements of atmospheric methane exceeded background atmospheric levels. We used sites with known methane emitters to determine the relationship between methane and co-emitted gases from those emission sources. We then used the ratios determined for biogenic and thermogenic (fossil) sources to calculate the contributions of these two processes to atmospheric methane from unknown hotspots and in the well-mixed urban airshed. Known methane sources were comprised of half biogenic and half thermogenic. Unknown sources were 15% biogenic and 85% thermogenic. The atmospheric methane concentration in the well-mixed air was only 5% biogenic. In total, we determined that more than two-thirds of local methane within the Los Angeles Basin urban airshed was "leakage" released from thermogenic sources.

Constraining the simultaneous effects of elevated CO₂, temperature, and shifts in rainfall patterns on ecosystem carbon fluxes using multi-scale resource optimization theories

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Increases in atmospheric carbon dioxide concentrations (c_a) leads to changes in the climate that alter mean air temperature (T_a) and precipitation (P) patterns. The ability of terrestrial ecosystems to absorb c_a is sensitive to these climatic conditions, as well as to c_a , thereby creating a feedback that has the potential to accelerate warming. To describe the feedback, the primary pathways by which elevated c_a , T_a , and changing P patterns simultaneously impact ecosystem photosynthesis and respiration must be quantified. Our objective is to produce a synthesis that capitalizes on the strengths of different models and incorporates the important feedbacks of the soil-plant-atmosphere system at pertinent spatial and time scales. Our progress report to DOE will highlight the completed tasks. This presentation focuses on one completed task - a novel theoretical link between plant-water use strategies and parameters describing responses of stomata to their environment via stomatal optimizing theories. Optimization theories have been used to explain a variety of forms and functions in plants. At the leaf scale, it is often hypothesized that carbon gain is maximized, thus providing a quantifiable objective for a mathematical definition of optimality conditions. Eco-physiological trade-offs and limited resource availability introduces natural bounds to this optimization process. In particular, carbon uptake from the atmosphere is inherently linked to water losses from the soil as water is taken up by roots and evaporated. Hence, water availability in soils constrains the amount of carbon that can be taken up and assimilated into new biomass. The problem of maximizing photosynthesis at a given water availability by modifying stomatal conductance, the plant-controlled variable to be optimized, has been traditionally formulated for short time intervals over which soil moisture changes can be neglected. This simplification led to a mathematically open solution, where the undefined Lagrange multiplier (or marginal water use efficiency - MWUE) is heuristically determined via data fitting. A set of models based on different assumptions that account for soil moisture dynamics over an individual dry-down are proposed so as to provide closed analytical expressions for the carbon gain maximization problem. These novel solutions link the observed variability in MWUE over time, across soil moisture changes, and at c_a concentrations to water use strategies ranging from intensive, in which all soil water is consumed by the end of the dry-down period, to more conservative, in which water stress is avoided by reducing transpiration.

Coupling Peat Decomposition and Metagenomics to Incorporate Molecular Scale Processes into Climate Models

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The goal of this project is to investigate changes in the structure of dissolved and solid phase organic matter, the production of CO₂ and CH₄, and the composition of decomposer microbial communities in response to the climatic forcing of environmental processes that determine the balance between carbon gas production versus storage and sequestration in peatlands. Cutting-edge analytical chemistry and next generation sequencing of microbial genes has been applied to habitats at the Marcell Experimental Forest (MEF), where the US DOE's Oak Ridge National Laboratory and the USDA Forest Service are constructing a large-scale ecosystem study entitled, "Spruce and Peatland Responses Under Climatic and Environmental Change"(SPRUCE). Our study represents a comprehensive characterization of the sources, transformation, and decomposition of organic matter in the S1 bog at MEF. Multiple lines of evidence point to distinct, vertical zones of organic matter transformation: 1) the acrotelm consisting of living mosses, root material, and newly formed litter (0-30 cm), 2) the mesotelm, a mid-depth transition zone (30-75 cm) characterized by labile organic C compounds and intense decomposition, and 3) the underlying catotelm (below 75cm) characterized by refractory organic compounds as well as relatively low decomposition rates. These zones are in part defined by physical changes in hydraulic conductivity and water table depth. O-alkyl-C, which represents the carbohydrate fraction in the peat, was shown to be an excellent proxy for soil decomposition rates. The carbon cycle in deep peat was shown to be fueled by modern carbon sources further indicating that hydrology and surface vegetation play a role in belowground carbon cycling. We provide the first metagenomic study of an ombrotrophic peat bog, with novel insights into microbial specialization and functions in this unique terrestrial ecosystem. Vertical structuring of microbial communities closely paralleled the chemical evolution of peat, with large shifts in microbial populations occurring in the biogeochemical hotspot, the mesotelm, where the highest rates of decomposition were detected. Stable isotope geochemistry and potential rates of methane production paralleled vertical changes in methanogen community composition to indicate a predominance of acetoclastic methanogenesis mediated by the Methanosarcinales in the mesotelm, while hydrogen-utilizing methanogens dominated in the deeper catotelm. Preliminary evidence suggests that the availability of phosphorus limits the microbially-mediated turnover of organic carbon at MEF. Prior to initiation of the experimental treatments, our study provides key baseline data for the SPRUCE site on the vertical stratification of peat decomposition, key enzymatic pathways, and key enzymatic pathways.

Coupled active and passive remote sensing to describe the land surface of piñon-juniper ecosystems

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The recent climate in the southwestern US has been punctuated by severe, climate change related drought events. These droughts are characterized by high temperatures coupled with very low precipitation, and result in widespread coniferous tree mortality. Piñon juniper (PJ) woodlands account for > 11% of the land cover in NM alone, and the mortality these systems are currently experiencing may result in an ecosystem state change unprecedented in recent history. Given the extent and severity of the woody mortality in PJ systems, it is essential that we improve our ability to characterize the variability in ecosystem structure exhibited by these heterogeneous ecosystems and constrain the uncertainty in PJ woodland biomass estimation in the context of severe, widespread forest mortality.

We have been tasking multi-temporal high resolution satellite data from WorldView-2 in an attempt to increase our understanding of the variability in canopy reflectance in both intact and disturbed PJ woodlands. We also have acquired full waveform aerial lidar flown for overlapping regions, allowing a detailed spectral and structural description of the PJ land surface. This multi-sensor data integration coupled with ground based field plot validation has improved our ability to: i) create thematic classifications of the vegetation cover in PJ systems, ii) describe the PJ land surface as a distribution of structural traits such as leaf area and canopy height, and iii) provided a framework with which to investigate the capability of combined active and passive data sources to scale biomass estimates from the field plot to the region.

We quantified the contributions from each sensor to the overall users and producers accuracy in our thematic products using a variety of classification algorithms, and discuss the strengths and weaknesses of each approach. We also used our data rich environment to create descriptions of ecosystem state parameters like canopy height and LAI, but describe them in the context of their spatial distribution as a function of disturbance. This allows us to generate hypotheses about how not only the mean of these parameters will vary with disturbance (e.g., decrease in mean canopy height following piñon mortality), but also the parameter variance. In this way we can describe the trajectory of ecosystem properties in the context of widespread mortality. Finally, we describe our current capability to scale plot estimates of PJ biomass to the region using an object oriented approach.

Responses of subalpine tree recruitment to warming within and above current altitudinal ranges

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Objectives: High latitude and high elevation forests are globally important contributors to carbon storage and release, and have strong regional leverage on surface energy balance and water fluxes. Highly uncertain feedbacks to climate change from dynamic shifts in forest distributions are increasingly incorporated into Earth system models, but lack data for parameterizations and quantitative benchmarks. We established the Alpine Treeline Warming Experiment at Niwot Ridge, CO, to examine effects of climate warming on tree seedling establishment near the lower limit of subalpine forest, at upper treeline, and in the alpine. We use infrared heaters to increase surface temperatures, and to lengthen the growing season. The warming treatment is crossed with a soil moisture manipulation to distinguish effects due to higher temperatures from those due to drier soil. Each plot is a common garden sown with two populations each of three species. We are asking: Will subalpine trees move into current alpine habitat and/or be impaired in their existing range as a result of climate change? And how do ecophysiological and population genetic factors influence changes in subalpine species success?

Results: During 2010-2013, heating elevated soil temperatures, with larger increases (~ 4.5 °C) in forest, than in alpine and treeline (1.5-2 °C) sites, reflecting differences in wind speed and heater efficiency. Heating alone tended to slightly reduce soil moisture, while heated and watered plots were not systematically wetter or drier than controls, as intended. In 2012, heating advanced snowmelt dates by 10-40 days. Preliminary analyses show that heating reduced germination for two species and, in most years, had no or negative effects on survival to 2 years in the forest, while watering increased demographic rates, consistent with expectations of reduced recruitment at lower elevations with warming and drying. At treeline, heating also reduced germination, but had year-dependent effects on survival to 2 years. In the alpine, contrary to expectations, experimental heating did not increase germination or survival, while watering increased survival to two years. In alpine and treeline sites, ecophysiological and microclimate measurements indicate increased exposure of seedlings to summer water stress with warming, resulting in lower net carbon assimilation that offset increased assimilation due to reduced cold stress. Observed differences among species in temperature and moisture thresholds may explain differences in response to treatments. Meta-population models offer an opportunity to bridge experimental results to landscape scales and establish benchmarks for shifts in forest tree distributions with climate change.

The effects of climate, forest age, and disturbance history on carbon and water processes at AmeriFlux sites across gradients in Pacific Northwest forests

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We investigated climatic and hydrologic effects on terrestrial ecosystem carbon and water processes across a climatic gradient and age class gradient in important forests (i.e., mature ponderosa pine, US-Me2, young ponderosa pine, US-Me3, and mature Douglas-fir, US-MRf) in the Pacific Northwest, USA. US-Me2 and US-Me3 are semi-arid forests with seasonal drought, whereas US-MRf is a mesic forest with high winter precipitation. We conducted eddy covariance measurements to measure carbon and water balances over 20 site-years and used hydrological year to define seasons and explain annual variation. Annual net ecosystem CO₂ exchange (NEE) at US-Me2 (2003-2012), US-Me3 (2005-2009), and US-MRf (2007-2011) varied from -571 to -248, from -160 to -19, and from -601 to -313 g C m⁻² yr⁻¹, respectively. Annual evapotranspiration (ET) ranged from 410 to 687, from 342 to 418, and from 369 to 521 mm yr⁻¹ for the same period. On average (2005-2009), US-Me2 had 5.0 times larger NEE and 1.4 times larger ET than US-Me3 due to higher leaf area index (LAI) and more available soil water from precipitation. Despite lower LAI and precipitation at US-Me2, difference in climatic gradient (e.g., higher radiation and evaporative demand) at US-Me2 resulted in a similar NEE and 1.4 times larger ET than US-MRf for the 5-year period (2007-2011). The annual average inherent water use efficiency (IWUE) at US-Me2, US-Me3, and US-MRf varied from 2.0 to 3.7, from 2.0 to 3.6, and from 2.4 to 3.9 g C kPa per kg H₂O, respectively. The variation in the annual IWUE at the drought-affected US-Me2 and US-Me3 was correlated with precipitation and vapor pressure deficit (VPD), whereas IWUE at US-MRf was constrained by VPD and had no correlation with precipitation. The trend of the anomaly of the annual IWUE (Δ IWUE) at US-Me2 and US-Me3 was a decreasing slope of -0.13 and -0.10 g C kPa per kg H₂O yr⁻¹, respectively. In contrast to the two ponderosa pine sites, Δ IWUE at US-MRf showed an increasing trend of 0.35 g C kPa per kg H₂O yr⁻¹. The trends of Δ IWUE at the three sites were primarily associated with the changes in ET rather than gross primary production. The increased ET at US-Me2 and US-Me3 resulted in decreased Δ IWUE, whereas the decreased ET at US-MRf resulted in increased Δ IWUE. Our study suggests that climate projection with higher temperature and evaporative demand in the Pacific Northwest will shift carbon and water balance of the forests by altering ET.

Collaborative Research on Ecophysiological controls on Amazonian precipitation seasonality and variability

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The Amazon currently plays a critical role in the terrestrial climate system. Over the last decade, Amazonian forests have begun experiencing more frequent dry periods, including two extreme drought episodes in 2005 and 2010. However, the future of the Amazon as projected by current generation climate or earth system models is highly uncertain: how global warming and other aspects of anthropogenic change such as deforestation and degradation will ultimately impact this system is far from clear. A dominant source of uncertainty regarding Amazonian climate and its future evolution is the role of land-vegetation-atmosphere coupling, especially interactions between vegetation and precipitating deep convection occurring during the late dry season/early wet season when land-vegetation-atmosphere coupling has been shown to be stronger. Quantitative understanding of this coupling is critical since forest productivity is sensitive to the duration and intensity of the dry season. Thus, in the present proposal, our principal objective 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 support this objective, our proposed research comprises three interrelated activities: (i) in situ measurements of plant physiological water stress with a focus on fluorescence and its control on surface energy and water budgets as observed at existing flux tower sites; (ii) diagnostic analysis of plant physiological parameters and processes, observed surface turbulent fluxes, boundary layer properties, and cloud cover and precipitation along a moisture gradient; and (iii) process- based model studies of the pathways through which the surface energy partitioning (Bowen ratio) and transpiration, as modified by water stress, influence convection both locally and non-locally.

We have incorporated equations for SIF into a land surface model, the National Center for Atmospheric Research Community Land Model version 4 (NCAR CLM4), to better estimate terrestrial GPP. First, we use existing theory and data to explain how SIF was incorporated into CLM4.. We then demonstrate that our simulated fluorescence values are reasonable when compared with satellite (Greenhouse gases Observing SATellite; GOSAT) and in situ flux-tower measurements. Our results overestimate GPP in tropical forests and thus indicate that maximum carboxylation rate, V_{max} , may be too high in tropical forests. Photosynthesis influences energy, water and carbon cycles, and we expect that the incorporation of SIF, along with satellite and in situ measurements, will improve estimates for GPP and thereby play a critical role in improving land

Evaluation and Improvement of Terrestrial Carbon Cycle Models With Observations

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Terrestrial carbon cycle is a critical component of global carbon cycle in response and feedback to climate change. Yet most model evaluation studies conducted so far all indicate that Earth system models predict terrestrial carbon cycle poorly. Research in my lab has focused on evaluating and improving terrestrial carbon cycle models with observations.

We have improved the modeled turnover rates of the surface leaf litter against a global observed dataset of litter turnover rates using a Bayesian Markov Chain Monte Carlo (MCMC) approach to calibrate the model. After data assimilation, the model explained 43% of spatial variability in the observed litter turnover rates, which was better than the initial 15%. Data assimilation selects litter quality limitation function to be dependent on litter lignin-to-nitrogen ratio instead of the structural lignin content. The new model structure explained 61% of variability in the observations.

We improved the simulation of soil organic carbon (SOC) storage in CLM-CASA'. The original CLM-CASA' on average underestimated SOC pools by 65% ($r^2=0.28$). We applied data assimilation to CLM-CASA' to estimate SOC residence times, C partitioning coefficients among the pools, and temperature sensitivity of C decomposition. The model with calibrated parameters explained 41% of the global variability in the observed SOC, which was substantially better than the initial 27%. The projections differed between models with original and calibrated parameters: over 95 years the amount of C released from soils reduced by 48 Pg C.

We also calibrated two microbial model formulations to global total soil organic carbon and microbial biomass pools, and compared the models' performance to that of CLM-CASA'. Once calibrated, both microbial models explained 51% of variability in the observed soil carbon. Maximum likelihood magnitude of SOC decrease after 95 years of climate change was almost 5-fold higher in the microbial models than in CLM-CASA'.

We applied a data assimilation approach to extract information from soil incubation data to constrain earth system models. A three-pool C-cycling model was optimally fitted with data from a 588-day long soil incubation experiment conducted at two temperatures (25 and 35 oC) for 12 soils collected from six sites arrayed across a mean annual temperature gradient from 2.0 to 25.6 oC. Initial C pool fractions were well constrained. Q10 values increased with recalcitrance of soil fraction. Higher Q10 for decades-old C fractions implies that a major portion of soil C may become a source of atmospheric CO₂ under global warming.

Control of Sphagnum-Derived Dissolved Organic Matter on Methane Production in Peatland Soils

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Peatlands are important ecosystems in the global carbon cycle serving as the largest terrestrial soil carbon pool and a significant source of the greenhouse gas CH₄. In Sphagnum-dominated wetlands, production of CH₄ is variable and controlling factors are poorly understood. Our objective was to determine if Sphagnum chemistry controlled CH₄ production across three Sphagnum-dominated soils with variable CH₄ production.

Soils were incubated anaerobically for 40 days with Sphagnum-derived dissolved organic matter (S-DOM) extracted with water at 25 or 60°C in a fully-crossed experimental design, and monitored for CO₂, CH₄, DOC, and phenolic concentrations. Hot extracts contained greater DOC and phenolics relative to cold extracts and stimulated CO₂ production in all soils. One soil produced no CH₄ during the incubation, regardless of S-DOM addition. However, site-specific inhibition or stimulation of CH₄ production was observed following S-DOM addition in remaining soils. High CO₂:CH₄ in hot extract amended soil suggests S-DOM was available to microbes, but not utilized by methanogens. These data suggest Sphagnum chemistry alone does not explain low CH₄ production, but can be a controlling factor in some peatlands.

Fluxes of CO₂, CH₄, CO, BVOCs, NO_x, and O₃, in an old growth Amazonian forest

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Tropical forests hold a large store of carbon that is rapidly exchanging with the atmosphere through prolific photosynthesis and respiration. Tropical forest vegetation is very large source of biogenic hydrocarbons and tropical soils have high emissions of nitrogen oxides. Agricultural and urban development with its associated biomass burning further add to the emission of reactive trace gases. The close coupling of carbon cycling and atmospheric chemistry give this region critical influence on the global environment. Carbon flux measurements have been made at a site in the Tapajos National Forest near Santarem (the Tapajos km67 site) since 2002. In order to provide an upwind complement to the intensive atmospheric chemistry and aerosol measurements sited near Manaus we are continuing the carbon flux measurements and adding new observations of key atmospheric trace gas concentrations and fluxes. Our new measurement suite includes; NO_y concentrations and eddy fluxes, NO/NO₂, O₃, CH₄, and SO₂ concentration profiles. During intensive campaigns scheduled for when the instruments are not needed for IOP in Manaus we will install PTRMS for hydrocarbon measurements.

The electrical supply to the site was rebuilt in the past year to repair some safety and reliability issues caused by storms and aging. Work included repair of the existing system to operate the CO₂ flux and profile measurements. The site infrastructure was rebuilt to provide clean space for new instruments such as the PTRMS and to provide an in situ space for sample and data analysis. The instrument package with NO_y and NO/NO₂ analyzers together with data acquisition/control system and sample flow handling has been integrated and tested. It was shipped to Brazil and has now cleared customs and scheduled for delivery in Santarem. We will begin installation at the km67 site the week of April 14, and anticipate having valid measurements available in early May. These will run continuously thereafter.

Analysis of the CO₂ flux data indicate the Tapajos km67 stand has been a net carbon source for 2009-2011, despite a lack of a significant disturbance in the recently preceding years. Variations in carbon exchange over the 7.5 years of observation can be well predicted by simple empirical relationships to radiation inputs and the duration of wet and dry seasons. Anomalies from this relationship such as the net CO₂ emission in 2002 when the model predicted carbon neutral or a small carbon sink can identify ecological perturbations such as a large-scale disturbance.

Aquaporin-Mediated Reduction in Root Hydraulic Conductivity Impacts Whole Stand Water Use and Carbon Assimilation: Scaling and Modeling the Effect of Sea Level Rise from Roots to the Ecosystem

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Due to a combination of thermal expansion of seawater and melting of polar ice sheets, global sea level rose 0.17 m over the 20th century and is projected to rise by at least 0.45 m by 2100. Unmanaged ecosystems along the Atlantic and Gulf coastal plains are especially vulnerable to sea level rise (SLR). In addition to constant flooding, SLR is expected to foster high salinities into tributary freshwater areas of the coastal zone. The current understanding of plant adjustment and tolerance to flooding and salinity is that they affect the plant conducting system in order to maximize water uptake. Although, understanding plant responses to SLR requires the determination of what affects physiological responses to the stressors, there are no studies that have focused on variation in plant hydraulic traits. Water flow in the soil-plant-atmosphere continuum is determined by the whole-tree hydraulic conductance of soil and plant tissues (K_{tree}), which characterizes the capacity of the plant at moving water. We showed that 50-60% of the whole-plant hydraulic resistance ($1/K_{tree}$) is located in the root system ($1/K_{root}$), stressing the outstanding importance of this organ within the flow path. In addition, recent work demonstrated that aquaporin (AQP = membrane protein) activity is the primary factor determining radial conductivity of roots in response to a large variety of environmental factors. Using a high pressure flow meter and hydroxyl radical inhibition of AQPs, we have found that flooding and salinity reduced K_{root} and AQP activity of roots of *P. taeda* grown in a controlled greenhouse. Our study indicated that water transport by AQPs accounted for 20% to 85% of the overall water transport. These results also showed that the inhibition of AQP was higher in control trees, indicating that flooding and salinity reduced the AQP contribution to K_{root} . AQP-induced inhibition of K_{root} affected plant water transport by reducing K_{tree} by more than 28%, and stomatal conductance by 25% under flooded condition and 55% under flooded +salt condition. Furthermore significant reduction in K_{root} and thus K_{tree} caused plants to transpire less, significantly altering microclimatic conditions in the canopy boundary layer. Using a mechanistic soil-plant-atmosphere model (SPA) and our empirical data we predicted that SLR would reduce water uptake by 55% and gross ecosystem productivity by 31%. Those predictions were consistent with the reduction in tree growth measured in the field and with the measured water (sap flow) and carbon fluxes (eddy covariance).

How well do stomatal conductance models perform on closing plant carbon budgets? A test using seedlings grown under current and elevated air temperatures

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Future carbon and water fluxes within terrestrial ecosystems will be determined by how stomatal conductance (g_s) responds to rising atmospheric CO_2 and air temperatures. While both short- and long-term CO_2 effects on g_s have been repeatedly studied, there are few studies on how g_s acclimates to higher air temperatures. Six g_s models were parameterized using leaf gas exchange data from black spruce (*Picea mariana*) seedlings grown from seed at ambient (22/16 °C day/night) or elevated (30/24 °C) air temperatures. Model performance was independently assessed by how well carbon gain from each model reproduced estimated carbon costs to close the seedlings' seasonal carbon budgets, a 'long-term' indicator of success. A model holding a constant intercellular to ambient CO_2 ratio and the Ball-Berry model (based on stomatal responses to relative humidity) could not close the carbon balance for either treatment, while the Jarvis-Oren model (based on stomatal responses to vapor pressure deficit, D) and a model assuming a constant g_s each closed the carbon balance for one treatment. Two models, both based on g_s responses to D , performed best overall, estimating carbon uptake within 10% of carbon costs for both treatments: the Leuning model and a linear optimization model that maximizes carbon gain per unit water loss. Since g_s responses in the optimization model are not a priori assumed, this approach can be used in modeling land-atmosphere exchange of CO_2 and water in future climates.

On the complementary relationship between marginal nitrogen and water use efficiencies among *Pinus taeda* leaves grown under ambient and enriched CO₂ environments

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Water and nitrogen (N) are two limiting resources for biomass production of terrestrial vegetation. Water losses in transpiration (E) can be decreased by reducing leaf stomatal conductance (g_s) at the expense of lowering CO₂ uptake (A), resulting in increased water use efficiency. However, with more N available, higher allocation of N to photosynthetic proteins improves A so that N use efficiency is reduced when g_s declines. Hence, a tradeoff is expected between these two resource use efficiencies. We hypothesize that when foliar N varies on time scales much longer than g_s , an explicit complementary relationship between the marginal water and N use efficiency emerges. Furthermore, a shift in this relationship is anticipated with increasing atmospheric CO₂ concentration (c_a).

We employ optimization theory to quantify interactions between resource use efficiencies under elevated c_a and soil N amendments. The analyses are based on marginal water and nitrogen use efficiencies, MWUE and MPNUE, respectively. The relationship between the two efficiencies and related variation in intercellular CO₂ concentration (c_i) were examined using A- c_i curves and foliar N measured on *Pinus taeda* needles collected at various canopy locations at the Duke Forest Free Air CO₂ Enrichment experiment (North Carolina, USA).

Optimality theory allowed the definition of an explicit relationship between two intrinsic leaf-scale properties where MPNUE is complementary to the square-root of MWUE. Our data support the model predictions that elevated c_a increased MPNUE and MWUE, and at given c_a and needle age-class, the two quantities varied among needles in approximately complementary manner. The derived analytical expressions can be employed in scaling-up carbon, water, and nitrogen fluxes from leaf to ecosystem, but also to derive transpiration estimates from those of nitrogen use, and assist in predicting how increasing c_a influences ecosystem water use.

Modeling complex ecosystem carbon-nitrogen cycle dynamics after disturbance

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Disturbance is a universal feature of terrestrial ecosystems that reorganizes soil and biomass pools, typically in a configuration away from the natural mode of variability. For example, disturbances such as fire or hurricanes transfer a substantial amount of carbon and nitrogen from live vegetation to dead litter, thereby altering ecosystem function. As another example, reforestation of abandoned agricultural fields can be considered a disturbance to the mature forest dynamics. Seeding, fertilization, harvest, and other intensive management practices lead to an initial non-forest state that precedes reforestation (i.e., the transition from the disturbed to the mature state). In this poster, we address the modeling of these initial transients in ecosystem dynamics and, in particular, the conditions for non-linear disturbance responses in soil and plant carbon and nitrogen pools.

The analysis presented here synthesizes 2 models of varying complexity with observations collected during reforestation of the Calhoun Experimental Forest in the South Carolina Piedmont. The data reveal distinct oscillations between plant and soil nitrogen pools, commonly referred to as “overshoot.” First, we show that this non-linear behavior occurs during initial transients, even when model stability analysis suggests the underlying model dynamics are not complex. Second, we analytically derive the conditions for overshoot at Calhoun from a reduced-order model. These conditions suggest a strong dependence on the system initial conditions, which reflect the agricultural land use legacy. Last, we introduce a second example of overshoot observed in semi-arid grassland in response to simultaneous drought and fire. In this case, a fertilization experiment confirms the role of anthropogenic factors in the ecosystem disturbance response. In summary, we conclude: (1) overshoot in ecosystem soil and biomass pools following disturbance may be relatively common; (2) the occurrence and magnitude of overshoot depends on initial conditions set by land management practices; and (3) the interpretation of disturbance responses requires analysis of both steady-state and transient dynamics.

Effects of disturbance on carbon sequestration in the New Jersey Pine Barrens

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Disturbance affects tree and ecosystem functioning and has the potential to alter water use, carbon uptake and respiration rates. We studied both biogenic (insect defoliation) and anthropogenic (prescribed fire) disturbance effects on carbon and water cycling in forested stands (pine- and oak-dominated) within the New Jersey Pine Barrens. This research becomes particularly important as climate change may increase the occurrence of insect defoliation in northern forests and increasing suburbanization necessitates the prevention of widespread wildfires with prescribed burning. To determine the effects of prescribed fire, we measured sap flow rates and gas exchange to estimate leaf- and canopy-level stomatal conductance in three stands experiencing an early-spring burn and three nearby control sites. We found that effects of prescribed fire were transient, and were only evident during the growing season of the burn year. Likewise, effects of prescribed fire differed between pine- and oak-dominated forests. Trees in oak-dominated forests exhibited decreased stomatal conductance following prescribed fire, whereas trees in pine-dominated forests exhibited increased stomatal conductance. Prescribed fire in pine-dominated forests also led to short-term increases in rubisco-limited carboxylation rate (V_{cmax}) and intrinsic water use efficiency. In contrast to prescribed fire, gypsy moth defoliation caused longer lasting effects on forest carbon sequestration with a 25% loss in overstory oak basal area. In order to characterize the effects of this mortality, we made spot measurements of respiration rates of dead trees (snags and coarse woody debris) and modeled stand-level respiration rates from dead stems at a fine temporal scale using environmental parameters and forest inventory and analysis (FIA) datasets. We found that the mass of dead stems increased five-fold after defoliation and respiration rates increased more than three-fold. The contribution of dead stems to total ecosystem respiration more than tripled from 0.85% to almost 3% and respiration from dead stems alone was approximately equal to the net ecosystem exchange of carbon dioxide for the stand in 2011 (fourth year post-disturbance). In total, this research highlights the importance of forest type in determining disturbance effects as well as the length of time that a given disturbance will affect ecosystem function. Furthermore, forest response to disturbance varies from the leaf to the ecosystem level as well as between species and these differential responses interplay to determine the fate of forest structure and functioning. These results will aid in the parameterization of ecosystem models in light of disturbance regimes.

Interactive effects of climate change and decomposer communities on the stabilization of wood-derived carbon in soils: Catalyst for a new study

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Globally, forest soils store ~two-thirds as much carbon (C) as the atmosphere. Although wood makes up the majority of forest biomass, the importance of wood contributions to soil C pools is unknown. Even with recent advances in the mechanistic understanding of soil processes, integrative studies tracing C input pathways and biological fluxes within and from soils are lacking. Therefore, our research objectives were to assess the impact of different fungal decay pathways (i.e., white-rot versus brown-rot) - in interaction with wood quality, soil temperature, wood location (i.e., soil surface and buried in mineral soil), and soil texture - on the transformation of woody material into soil CO₂ efflux, dissolved organic carbon (DOC), and soil C pools. The use of ¹³C-depleted woody biomass harvested from the Rhinelander, WI free-air carbon dioxide enrichment (Aspen-FACE) experiment affords the unique opportunity to distinguish the wood-derived C from other soil C fluxes and pools.

Progress to date includes: 1.) Established treatment plots across six field sites (three sand and three loam textured soil) with Aspen-FACE wood chips inoculated with white rot (*Bjerkandera adusta*) and brown rot (*Gloeophyllum sepiarium*) fungal cultures; 2.) Cored soils to 30 cm in 0-15 cm and 15-30 cm segments and analyzed soils for initial stable carbon isotope values and CN concentrations; 3.) Instrumented treatment plots with lysimeters, temperature data loggers, and open-topped, passive warming chambers; 4.) Initiated laboratory incubations to test the effect of wood quality and fungal inoculation on CO₂ flux rates and isotopic signatures of wood and CO₂; and 5.) Measured soil ¹³CO₂ efflux, DO¹³C over one growing season.

Initial conditions for soil $\delta^{13}\text{C}$ values and CN concentrations averaged across the six sites were -26.8‰ (standard error = 0.04), 2.46% (se = 0.11), and 0.15% (se = 0.01), respectively. The labeled wood chips from the Aspen FACE treatments had an average $\delta^{13}\text{C}$ value of -39.5‰ (se 0.10). The >12 ‰ isotopic difference between the soil and wood chip $\delta^{13}\text{C}$ values provides the basis for tracking the wood-derived C through the early stages of decomposition and subsequent storage in the soil. Results from our first year of field soil CO₂ efflux measurements indicate that fungal pathways and wood placement (i.e., surface versus buried) have an impact on the soil CO₂ flux rates. A greater proportion of white rot fungal treatment soil CO₂ efflux comes from wood-derived C compared with that of brown rot treatments, 50% and 39%, respectively.

Determining the Drivers of Redox Sensitive Biogeochemistry in Humid Tropical Forests

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The availability of soil O₂ and associated redox dynamics are key drivers of C cycling and greenhouse gas fluxes in tropical forests. Changes in climate are likely to affect soil O₂ availability in tropical forests and feedback on ecosystem biogeochemistry. Few studies have measured soil O₂ availability over time and space in tropical forests, and thus this important parameter is absent or poorly represented in Earth systems models. In this study we will use field and laboratory experiments in humid tropical forests to develop a mechanistically derived redox component for the Community Land Model (CLM4) component of the Community Earth System Model (CESM). We will use our empirical and modeling efforts to improve the prediction of C, N, and P cycling and greenhouse gas dynamics in humid tropical forests. Our research will test the following hypotheses:

H1: Soil O₂ concentrations vary as a function of soil texture, slope position, and rainfall in humid tropical forests.

H2. The spatial and temporal dynamics of soil O₂ availability can be used to predict patterns in redox sensitive biogeochemical processes.

H3. Hot spots and hot moments in greenhouse gas fluxes are derived primarily from high substrate availability and secondarily from soil O₂ availability.

Research is being conducted in the Luquillo Experimental Forest (LEF), Puerto Rico. We are using controlled field and laboratory experiments to establish the relationships between soil O₂, climate, soil physical properties, and a range of redox sensitive biogeochemical processes including soil respiration, net and gross N₂O and CH₄ fluxes, and Fe redox impacts on P mobilization. We will use automated sensor and surface flux networks to test the hypotheses. We will also use fertilization experiments to determine the relative importance of substrate availability and soil O₂ concentration on gross and net greenhouse gas dynamics. Unlike previous efforts that have clearly established relationships among soil O₂ concentrations and redox couples, the objectives of this research are to determine the physical controls on soil O₂ availability and biogeochemical cycling to derive mechanistic relationships for modeling. The data will be used to improve the redox representation in CLM4. We will introduce new equations representing diffusion and source/sink behavior of O₂ with depth.

Isotopic Partitioning of CO₂ fluxes revises understanding of mechanisms of forest carbon sequestration

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Ecosystem models differ widely in their predictions of how forest carbon dynamics will interact with a changing climate, and that interaction is a large source of uncertainty in predictions of future climate. We are investigating the mechanisms controlling carbon allocation and sequestration at the Harvard Forest by integrating stable carbon isotope analyses with a suite of 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. Here we present some of this year's key results; other presentations at this meeting focus on the root measurements (Abramoff et al.) and the trenching experiment (Savage et al.).

Using eddy covariance measurements of the forest-atmosphere exchange of ¹²CO₂ and ¹³CO₂, we partitioned the net ecosystem-atmosphere CO₂ exchange (NEE) into photosynthesis and respiration on an hourly timescale - a longstanding goal in carbon cycle science. This partitioning revises our picture of the seasonal pattern of canopy photosynthesis at Harvard Forest, which increased through the summer and early fall despite concurrent declines in light, stomatal conductance, and leaf internal CO₂ concentration. In other words, canopy photosynthetic efficiency increased through the summer, counter to expectation from standard NEE partitioning approaches.

The isotopic partitioning also showed that ecosystem respiration declined with soil water content, a finding qualitatively corroborated by our chamber and fine root respiration measurements. More surprisingly, moisture was more limiting during the day than at night, perhaps due to local drawdown of soil water around the roots of transpiring trees. Due to these moisture effects, standard NEE partitioning models considerably overestimated ecosystem respiration and photosynthesis in hot and dry conditions.

The 10-day mean isotopic disequilibrium (i.e. the composition of photosynthates minus that of ecosystem respiration) was found to be fairly stable at +1 ‰ through the growing season. Thus seasonal variation is not a viable explanation for the longstanding sign discrepancy between models and observational studies. Additionally, the seasonal decline in isotopic discrimination at our site agrees with previous continental-scale observations, suggesting that Harvard Forest isotopic patterns might be representative of North American ecosystems more broadly.

We are assimilating these measurements into an isotopic version of ED2 to explore the implications of ecosystem carbon allocation mechanisms for carbon sequestration and feedbacks to climate.

Tower-mounted cameras validate remotely sensed “green-up” of Amazon forest photosynthesis and reveal mechanisms underlying the seasonality of tropical forest metabolism

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The relation between surface radiation, leaf phenology, and seasonality of forest photosynthetic metabolism and water relations is of central importance in global change ecology. However, the seasonal rhythms of tropical forests remain poorly understood: they are not well-represented by models, and their remotely-sensed seasonal expressions are, controversially, claimed to be artifacts of sun-satellite geometry. Here, we aim to scale from the phenology of individual tree crowns to ecosystem photosynthesis, and to ground truth satellite-derived seasonal patterns of vegetation indices (MODIS EVI) in two evergreen tropical forests with different seasonalities (short dry season in the Cuieras Forest Reserve near Manaus, and long dry season in the Tapajos National Forest near Santarem, Brazil).

We developed a classification scheme to decompose daily images of forest tree crowns from

tower-mounted three-channel cameras - a red, green, and near-infrared (RG,NIR) in the Santarem forest (2010-2012) and a red, green, blue (RGB) camera in the forest near Manaus (2010-2013). This generated time series of tree crown phenology events (leaf flushing and leaf drop) that are insensitive to artifacts of sun-sensor geometry or atmospheric contamination that may affect satellite remote sensing metrics. The camera-sensed leaf phenology is consistent with seasonal dry season green-up detected by remotely-sensed MODIS EVI in the equatorial Amazon, suggesting that these seasonal variations are not sensor artifacts.

To investigate underlying mechanisms of observed patterns, we combined camera-derived leaf phenology and litterfall observations to drive a simple 3-cohort model (with young, mature and old leaves) of leaf demography optimized (with $R^2 \gg 0.8$) to predict seasonality of eddy flux-derived photosynthetic Light-Use Efficiency (LUE). The demographic model predicted that leaf-cohort photosynthetic capacity increased with leaf age from young to mature leaves before declining for old leaves prior to litterfall. This predicted pattern was confirmed by age-dependent measurements (via Licor 6400) of leaf photosynthetic capacity (V_{cmax}).

Our results reveal the demographic and physiological mechanisms that underlie ecosystem-scale seasonal patterns in photosynthetic capacity observed by eddy flux towers and satellites. Future work funded by DOE, FAPEAM and FAPESP's GoAmazon program will integrate detailed observations from hyperspectral and thermal imaging cameras of the canopy, dynamic range radiometric images of incoming radiation, and fine-scale observations of sap flow, leaf water potential, and canopy chlorophyll fluorescence and photosynthetic capacity. This integration will use models (DIRSIG and FLIES models) to predict seasonalities of canopy reflectance and ecosystem-scale photosynthesis, and provide a basis to improve earth system models of vegetation-climate interactions.

The Impact of Permafrost Carbon Loss on the Carbon Balance of an Experimentally Warmed Tundra Ecosystem

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Approximately 1700 billion tons of soil carbon are stored in the northern circumpolar permafrost zone, more than twice as much carbon than currently contained 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. Yet, the rate and form of release is highly uncertain but crucial for predicting the strength and timing of this carbon cycle feedback this century and beyond. Here we report results from five 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). 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, in line with decadal trends of 'greening' tundra across the region. This response increased through the first four years of the experiment and then maintained this elevated level in year five, even though thaw depth continued to increase. 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 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. These results highlight the importance of winter processes in determining whether tundra acts as a C source or sink, and demonstrate the potential magnitude of C release from the permafrost zone that might be expected in a warmer climate. Furthermore, this initial response to warming quantifies the vulnerability of organic C stored in near surface permafrost to temperature change, and corresponds to the initial stages of permafrost degradation observed from a thaw gradient at a nearby location.

Multi-scale methane fluxes from Howland Forest: merging tower and chamber flux measurements.

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Forests dominate the global carbon cycle, but their role in methane (CH₄) biogeochemistry remains uncertain. Limitations in mesoscale sampling approaches have led to gaps in our knowledge of the CH₄ uptake and release dynamics from forested ecosystems and the environmental drivers that control them. These gaps have allowed for speculation over the potential contribution of forests, whether the soils or the trees themselves, to the global CH₄ cycle. Building on our previous two years of work, published in Shoemaker et al. (2014), we have added a full year of CH₄ flux data from 2013 to our analysis. The first two years lacked data from the late winter and spring (January through May), but now we show that measured spring fluxes from 2013 are consistent with the predictions we made using a neural network approach for 2011 and 2012. Precipitation and water table data from Howland forest in 2013 show that the summer months were significantly wetter than average, similar to 2011 conditions. We estimate that 2013 was a net positive source of CH₄ to the atmosphere, consistent with our conclusion that rainy summers lead to positive annual emissions. During 2013, methane fluxes were also quantified at the level of the soil surface using multiple automatic chambers within the footprint of the tower. Ongoing analysis is focused on merging these data streams to build a more complete understanding of forest CH₄ biogeochemistry, as well as constructing an appropriate scaling model. Thus far, we find no evidence to suggest that trees themselves play any significant role in CH₄ cycling at Howland Forest. Overall, we find the fluxes from 2013 show a similar annual pattern to that observed during 2011 and 2012 supporting conclusions that Howland forest is a net source of methane during wetter years and net sink for CH₄ during drier years. These results have important implications for understanding forest methane emissions and building appropriate models for methane emissions from similar forested ecosystems.

Developing surface-modified polymeric probes for the in-situ capture of plant root exudates

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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. The overall effect of the exudation is regulated not only by the exudation processes itself, but also by the chemical transformation that these exudates undergo in soil matrices. The biological functions of these plant inputs are tightly governed by their composition and molecular identity. Yet the molecular composition of the exudates and their transformation pathways in soil matrices has remained ever-elusive due to complex biotic and abiotic interactions. We developed polymeric probes through in-situ polymerization of poly(styrene-co-vinylbenzyl chloride-co-divinylbenzene) to elucidate the chemical environment of the soil to which the plant roots are exposed to. The probes were subjected to post-polymerization surface modifications to enhance the extraction and retention capacity of plant metabolites. The efficacy of these probes was tested in soil-systems and extracted compounds were analyzed using various gas/liquid chromatography tandem-mass-spectrometry platforms.

The unmodified polystyrene-divinylbenzene probes exhibited lower sorption affinity for monophenolic and flavonoid compounds with the overall partitioning coefficient <1 . Hypercrosslinking of the polymeric probes through an in-situ Friedel-Crafts alkylation significantly increased the surface area and the sorption capacity of the probes, resulting in >10 fold increase in the partitioning of the plant metabolites onto the probes. Scanning electron microscopy revealed extensive modification of the surface of the probes through hypercrosslinking, however the mechanical rigidity of the probes was affected during the hypercrosslinking. The probes exhibited a lower site specific sorption (slope of Freundlich adsorption isotherm close to unity) and percent recovery of the sorbed compounds from the probes were >70 , indicating a predominance of reversible sorption. Polymeric probes coupled with mass spectrometry analysis enables us to capture and identify more than 50 metabolites (<1 kDa) from the soil matrices in a forested ecosystem. The flavonoid glycosides exhibited significantly lower sorption affinity to the probes than their respective aglycones indicating a potential biasness of probes towards hydrophobic metabolites. Increasing the molecular specificity of the probes through template impregnation and surface grafting will be attempted.

Up-rooting surface-atmosphere exchange models: How mycorrhizal associations may affect soil emission profiles

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Volatile organic compounds (VOCs) impact ecological interactions and atmospheric chemistry, but our understanding of the sources of and controls over VOCs from terrestrial ecosystems remains incomplete. Despite the potential for soil to be a significant source of VOCs, most emission models do not consider processes occurring at or below the soil surface. 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 VOC emissions. The primary aim of our project is to describe the mechanisms controlling soil VOC emissions within the context of plant-microbe interactions, forest nutrient cycling, and physical resistances to VOC transport to improve current mathematical descriptions of atmospheric photochemistry.

Using plots established across a mycorrhizal gradient within the Morgan Monroe State Forest, we are currently quantifying the magnitude, timing, and ecological and environmental controls of VOC emissions from forest soils. Once a month, samples are collected from chambers established within plots containing >90% AM or ECM-associated tree species (n=4). Air samples are collected using dynamic headspace techniques and compounds with m/z 21 to 140 are analyzed using proton transfer reaction-mass spectrometry (PTR-MS). Temperature and relative water content data and soil cores for enzymatic assays are also collected from soil + litter collars and collars where the litter has been removed.

Preliminary results from November 2013 show methanol to dominate emissions from both soil and litter (~20-30%), with the exception of acetaldehyde dominating litter VOCs in AM plots (~43%). Litter appears to be the primary source of fluxes observed late in the season and proportional differences of compounds to the total profile suggest that variation in litter type and microbial associations between ECM and AM plots are potentially translated into differences in VOC quality and quantity. We will continue to measure soil VOC emissions over time and look to correlate our findings with the abiotic and biotic factors being measured concurrently. We are also using state-of-the-art metabolomic techniques to explain the biochemical controls of observed soil VOCs and parse out sources of emissions within the rhizosphere. Our continued work will allow us to elucidate the unknown temporal variation of soil VOC fluxes in the context of environmental and biogeochemical conditions and gain valuable insight into biochemical controls over emissions and their potential role in atmospheric models.

A New Approach to Synthesizing Results from Global Change Experiments

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Plants and soils affect the climate, and how they respond to global change will shape future trajectories of climate change. Here we propose a new approach to test whether global change - elevated CO₂, warming and changes in precipitation affect the biological activity of plants and microbes, responses that could in turn feedback to reinforce or dampen changes in our climate. We use multiple data streams from global change experiments to constrain simple biogeochemical models, allowing us to estimate the effect of global change on model parameters which cannot be measured directly. Treatment effects on model parameters are then quantitatively summarized across different experiments by meta-analysis. We recently used this approach to show that although elevated atmospheric CO₂ increases the inputs of carbon to soil by 19.8%, it also increases the decomposition rate of soil organic matter by 16.5%, suggesting limited effects of atmospheric CO₂ enrichment on long term soil C storage. We also propose a similar, but more mechanistic approach using a model that includes a microbial and enzymatic link, allowing for potential feedbacks between microbial biomass and soil organic matter decomposition. We outline how our approach could be applied to numerous other questions related to plant-soil feedbacks to global change using more advanced biogeochemical models and different experimental manipulations.

Advancing our understanding of carbon-climate feedbacks in Arctic tundra: litter input controls on soil organic matter turnover and formation

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The Arctic has experienced substantial regional warming over the past 30 years that could turn the Arctic into a net source of carbon to the atmosphere as soil organic matter (SOM) decomposes. But in addition to temperature-driven acceleration of decomposition, several additional processes could either counteract or augment warming-induced SOM losses. For example, increased plant growth under a warmer climate will increase organic matter inputs to soils, which could fuel further soil decomposition by microbes, but will also increase the production of new SOM. Whether Arctic ecosystems store or release carbon in the future depends in part on the balance between these two counteracting processes, which this project focuses on. By differentiating SOM decomposition and formation and understanding the drivers of these processes, we will better understand how these systems function. We will integrate this new knowledge into a process-based biogeochemical model to improve our ability to forecast global change impacts on Arctic carbon stocks. Our project objectives are to (1) Improve our mechanistic understanding of Arctic climate-carbon feedbacks by evaluating how SOM priming and formation in Arctic tundra ecosystems are affected by plant C input chemistry and quantity, and temperature. (2) Characterize and quantify the net effects of long-term ecosystem warming on the molecular structure and distribution of C within SOM. (3) Characterize and quantify the mechanisms that lead to SOM priming and formation, and incorporate them in a scalable biogeochemical model integrated in CLM. (4) Evaluate the value of representing microbial controls over C cycling in a scalable biogeochemical model integrated in CLM and identify the measurements necessary to constrain uncertainty in predictions of SOM dynamics.

Partitioning Ecosystem Canopy Transpiration to Evaluate the Sensitivity Stomatal Conductance to Changing Climate Indicators.

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Two-thirds of terrestrial water fluxes to the atmosphere are through the process of transpiration (T), making this a key variable linking hydrological and biological processes. Transpiration is highly coupled with photosynthesis and is critical to modeling watershed hydrology and carbon uptake. The partitioning T from total evapotranspiration (ET) has been one of the greatest uncertainties in the water budgets of many ecosystem studies, owing to the lack of catchment scale measurements and large uncertainties in stomatal conductance. A major reason for this difficulty is that T is often derived as the residual of the water balance once other processes are explicitly measured or modeled.

Variations in the water balance across space and time are a function of interactions among species, environmental conditions, stand age, and management practices. However, evaluating the effects of environmental drivers on forest wetland ecosystems and the water budgets in coastal regions of the U.S.A. has not been the focal point of considerable research. Increasing variability of rainfall patterns and water table fluctuations requires a detailed understanding of the pathways of water loss from ecosystems to optimize carbon uptake, as well as land use and management choices.

At the Alligator River National Wildlife Refuge, eddy covariance, micro-meteorological and sap flux techniques were used to derive transpiration values from the four dominant overstory species (tupelo, bald-cypress, loblolly pine and red maple). Canopy transpiration represents more than 60% of total ET, a value significantly higher than in managed ecosystem. Canopy transpiration and stomatal conductance was highest in tupelo, followed by bald-cypress, red maple and then loblolly pine. Transpiration from subdominant trees and shrubs represented 20-35% of evapotranspiration. Indicating that understory was a significant part of the water budget. Annually, soil evaporation represented about 15% of evapotranspiration. Tree sensitivity to climate variables decreased under flooded periods with the tupelo being the most sensitive, altering water flux partitioning and carbon uptake.

The Prairie Heating and CO₂ Enrichment (PHACE) experiment: Synthesizing 8 years of data

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The Prairie Heating and CO₂ Enrichment experiment in native grassland near Cheyenne, Wyoming completed its final season of ecosystem manipulations in 2013. Our project is moving into final stages of data-model development and synthesis. Our principal goal was to understand direct and indirect effects of elevated CO₂ and climate warming on grassland biogeochemistry and community changes. Year-to-year precipitation inputs ranged two-fold, from 500mm in 2009 to 250mm in 2012. Precipitation variability was the primary driving factor for all the ecosystem processes examined. This is not surprising for this water-limited semi-arid grassland that receives on average about 400mm precipitation annually. However, elevated CO₂ (600 ppm) and experimental warming (+3C nighttime, +1.5C daytime) did have important effects. Our multi-year dataset is providing new insights into grassland responses to these global changes:

1) Effects of warming and elevated CO₂ on ecosystem greenness are seasonally variable, with warming enhancing greenness during wet periods and elevated CO₂ during dry periods. Yet these phenological differences balance to yield largely neutral effects over the entire growing season. 2) Plant species composition is relatively resistant to inter-annual variation in precipitation, and also rendered more stable under elevated CO₂ conditions. Increased stability derives from a decrease in the relative abundance of dominant species and increase in the relative abundance of subdominant species. 3) We calibrated a semi-mechanistic model of ecosystem respiration within a Hierarchical Bayesian framework. Modeled annual ecosystem respiration was stimulated under elevated CO₂ in most years of the project. Antecedent soil moisture content and soil temperature were critical factors for predicting ecosystem respiration. Indeed, most of the treatment differences were driven by antecedent conditions. 4) ¹⁴C measurements revealed that soil respiration derived from recent plant inputs was less temperature sensitive than soil respiration derived from soil organic matter. Further, decomposition of soil carbon >5 y years old increased with warming in the field and laboratory. The short mean residence time of new plant inputs, and evidence from a fallow experiment suggest that the effect of plant inputs on temperature sensitivity of soil respiration is short-lived. In contrast, sustained temperature sensitivity of slow-turnover soil carbon with an absence of new inputs suggests potential for soils to lose C with climate warming.

Taken together, the continuous set of annual observations and cumulative effects over 8-years of experimental manipulations has yielded critical insights into ecosystem dynamics and partitioning of global change effects from background variation in precipitation.

EMSL Poster Abstracts

Subsurface Conditions Controlling Uranium Retention Pathways

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Microbial uranium reduction in the subsurface can sequester substantial quantities of this toxic element, but the long-term fate depends upon the specific phases produced via reduction. Within natural environments, uranium often correlates with iron rather than existing as a discrete uranium oxide phase; uranium incorporation into iron oxides is a mechanism that can explain the co-occurrence of these two elements and may represent a natural attenuation pathway for uranium. Further, incorporated uranium within Fe (hydr)oxides appears stable with respect to oxidative dissolution, representing a potential means for long-term sequestration of uranium in the subsurface. Within this project we are examining uranium reduction pathways and mechanisms.

We have examined the divergent fate of uranium being either incorporated within iron oxides or reduced to U(IV) solids. Our experiments reveal that: U(V) is incorporated into Fe oxides, calcium concentration has a determining effect on the dominant reaction pathway, (iii) U incorporated into Fe oxides across a broad range of conditions. Uranium valence state was measured using x-ray photoelectron spectroscopy, and U sequestration mechanisms were identified and quantified using extended x-ray absorption fine structure (EXAFS) spectroscopy, x-ray powder diffraction, and transmission electron microscopy (TEM). Depending on the reaction conditions, 12 to 80% of total U is incorporated into goethite. Uranium incorporation was a particularly dominant retention pathway at U concentrations $\sim 50 \mu\text{M}$. However, Ca limits both incorporation of U(V) into Fe oxides and reduction to U(IV). Calcium exerts a progressive inhibition of reduction to U(V) or U(IV) even at Ca:Fe ratios in excess of 2.6, rendering greater proportions of aqueous U(VI). We deduce that through the formation of the dicalcium uranyl carbonate complex, Ca blocks that active electron transfer coordinate for Fe(II). A mass expression for the exchange of Fe-Ca in the ternary complex describes the regulatory role of calcium (and by association other ternary complexing divalent cations).

In sum, our results demonstrate that complex reaction pathway for uranium reduction and illustrate that U incorporation can be a major U retention pathway. Ultimately, it is critical to recognize that multiple retention processes of uranium will occur in the subsurface, which must be considered in the long-term fate of this hazardous element.

EMSL: A DOE Scientific User Facility for Terrestrial and Subsurface Science Research

Nancy Hess (nancy.hess@pnnl.gov) - EMSL (PI), Karl Mueller EMSL (Co-PIs).

Robust, predictive models of contaminant fate and transport in the subsurface require understanding and identification of key geochemical and biogeochemical reactions that control contaminant mobility. The ability to identify and adequately probe dynamic processes at the molecular to pore scale can provide information needed to accurately simulate these processes with computational models and incorporate them into reactive flow and transport models, an important goal of many SBR researchers who address the nation's environmental challenges and provides the scientific basis for the long term stewardship of nuclear waste. Linking of experimental and theoretical information from molecular to field scale requires the integration of diverse experimental and computational techniques and collaboration with experts from multiple disciplines. Similarly, TES researchers seek analogous molecular-scale insights into the carbon and other elemental cycles in the terrestrial ecosystem with the goal of providing mechanistic understanding of key processes that currently are poorly represented in biogeochemistry components of the Community Land Model.

EMSL, a DOE national user facility in Richland WA, provides integrated experimental and computational resources and expertise for scientific research and discovery in subsurface biogeochemical research to users free of charge. There are numerous capability sets that are particularly relevant for biogeochemical research. I) Next generation imaging and surface characterization experimental capabilities that can be used to provide the spatially resolved elemental analysis, oxidation state determination, chemical speciation, mineral identification, and microbe-mineral associations necessary for understanding the chemical fate and mobility of contaminants in the biogeochemical environment. II) Advanced spectroscopic capabilities for determining the speciation of metal ions and complexes on surfaces, in solution, or incorporated in mineral phases. III) Comprehensive quantitative proteomics/metabolomics platforms, whole transcriptome analysis platforms, platforms for gene expression profiling, small RNA analysis, novel transcript identification, and many genome- and epigenome-directed applications provide EMSL users extensive capabilities for unraveling the interplay between microbial communities and geochemistry. IV) An integrated suite of capabilities to support research in subsurface flow and transport from the micron to the intermediate scale. Users have access to experts who assist with all steps of the research process from pre-experiment modeling to hydraulic characterization, numerical modeling, and post-process analysis on custom-built flowcells.

EMSL's Radiochemistry Annex, which greatly expands the range of experimental capabilities for analysis of environmental samples contaminated with radionuclides, is now available to users. The new facility consists of approximately 6000 sq ft of lab space. The surface analysis-imaging suite contains FIB-SEM, TEM-EELS, SPM, XPS,

Pore-Scale and Continuum Simulation of Microfluidics Experiments on Reactive Transport and Multiphase Flow conducted at EMSL

Albert Valocchi (valocchi@illinois.edu) - University of Illinois, (PI), Charles J. Werth, Youneng Tang, Tory Boyd; University of Illinois at Urbana-Champaign; Haihu Liu; University of Strathclyde; Hongkyu Yoon; Sandia National Laboratory; Mart Oostrom; Tom Wietsma; Pacific Northwest National Laboratory; Changyong Zhang; Exxon-Mobil; (Co-PIs).

Advances in microfabrication and imaging technology have enabled direct observation of coupled flow and reaction process at the pore scale. A state-of-art user facility was developed at EMSL to enable direct application of these advances to the study of pore scale processes in groundwater and deep subsurface reservoirs. Similar advances in computing power and numerical methods allow for direct numerical simulation of pore-scale processes from first-principles without any adjustable parameters. Investigators at the University of Illinois have been collaborating with EMSL scientists to conduct pore-scale experiments and simulations to investigate a variety of processes, including mixing-controlled aqueous reactions, mixing-controlled precipitation, and multi-phase flow. These processes are important to understand for many science and engineering questions, including contaminant fate and transport, biogeochemical dynamics in the root zone, and geological sequestration of carbon dioxide. By combining pore-scale simulation and experiments we have studied the impact of pore geometry and flow rate on mixing, how mixing and solution composition affects precipitate mineralogy, stability, and pore blocking, and the impact of flow rate and pore geometry on two-phase saturation and interfacial area. Numerical modeling allows testing of hypotheses about fundamental reaction mechanisms provides a tool for upscaling.

Other Poster Abstracts

The DOE Joint Genome Institute--Advancing Energy & Environmental Science

Dan Drell (daniel.drell@science.doe.gov) DOE, Eddy Rubin Lawrence Berkeley National Laboratory (PI).

The U.S. Department of Energy Joint Genome Institute (DOE JGI) is a large-scale genomic user facility dedicated to aiding researchers in sequence-enabled science through the analysis of genomes of microbes, microbial communities, plants, fungi, and other targets relevant to DOE missions in bioenergy, carbon cycling and biogeochemistry. In 2013, the DOE JGI completed over 4,300 user-initiated projects and generated more than 70 trillion nucleotides of genome-sequence data from microbes and microbial communities, fungi, algae, and plants — the equivalent of 23,000 human genomes. The DOE JGI added 1,420 genomes to the public databases this past year.

Omics and Geochemistry: the ENIGMA 100-Well Survey

Terry Hazen (tchazen@utk.edu) - University of Tennessee, Knoxville (PI).

At the Department of Energy's Oak Ridge field site, over 20 years of historical and published data for more than 800 groundwater wells is available in a computer queryable database. In this study, we conducted a survey of 99 groundwater well clusters in order to (1) characterize key microbial populations at geochemically distinct locations, and (2) identify associations between environmental gradients and microbial communities. To optimize geochemical diversity, wells were selected using k-medians clustering to group 818 wells into 100 clusters by 14 geochemically similar measurements. At each well, in situ groundwater measurements were recorded and unfiltered and filtered groundwater samples were collected for both geochemical measurements and analysis of microbial communities. Nucleic acids were collected by filtering water through a 10.0 μ m pre-filter and 0.2 μ m-membrane filter and then extracted using a Modified Miller method. Evaluation of divergence of microbial communities across all the wells indicates the microbial communities are fairly distinct. Comparison of microbial communities within each well shows taxa are not as divergent compared to across all wells. Metadata correlations of all the wells show many of the geochemical parameters are independent of each other. To evaluate potential microbial-geochemical associations, a random forest classification system was used and trained on the OTU abundances to predict continuous values for each geochemical parameter. Results indicate that with careful design and a large dataset, the groundwater microbial community structure can be used to accurately predict the water geochemistry. This project is part of the ENIGMA (Ecosystems and Networks Integrated with Genes and Molecular Assemblies) Scientific Focus Area at LBNL (<http://enigma.lbl.gov>).

Evaluating the ACASA model as a tool for flux interpretation at 4 AmeriFlux Sites

Jessica Osuna (osuna2@llnl.gov) - Lawrence Livermore National Laboratory, Sonia Wharton (LLNL) (PI), J. Osuna (LLNL), R.D. Pyles (UC-Davis), M. Falk (UC-Davis), S. Ma (UC-Berkeley), D. Baldocchi (UC-Berkeley), K. Bible (U-Washington), S. Biraud (LLNL) (Co-PIs).

Many eddy-covariance flux sites are equipped with one measurement height above the canopy. Due to power requirements, instrument cost, and the maintenance involved it is often unrealistic to expand measurements across the full profile of the canopy. However, an understanding of the turbulence dynamics throughout the canopy could be valuable in interpreting flux data at measurement height. We apply a higher-order closure turbulence and flux model to 4 distinct flux sites in order to model fluxes and profiles of turbulence in and above canopies. We used the UC-Davis Advanced Canopy-Atmosphere-Soil Algorithm (ACASA) to study a range of ecosystems including a tall old-growth forest with a complex canopy (Wind River AmeriFlux), a two-layered oak savanna (Tonzi AmeriFlux), a grassland (Diablo AmeriFlux), and a wheat field (Southern Great Plains AmeriFlux). We modeled each ecosystem for at least the duration of the growing season. At each site, the model was reinitialized twice per month using data of soil moisture and temperature. We assess the conditions under which applying a complex model like ACASA is beneficial in interpreting within-canopy dynamics and flux signal quality. We describe ACASA performance at the 4 sites as well as the changes to the model and the tuning necessary to optimize performance for each of the unique sites. Novel improvements to the model include the incorporation of seasonal dynamics in leaf area index and photosynthetic capacity, adjustment of plant water use during seasonal drought, and adjustments for a clumped canopy.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-ABS-648474

Progress toward developing a novel mini tunable diode laser for measuring CO₂ fluxes in situ

Jessica Osuna (osuna2@llnl.gov) - Lawrence Livermore National Laboratory (PI), Mihail Bora, LLNL (Co-PIs).

We introduce a novel mini tunable diode laser (TDL) that is being developed at Lawrence Livermore National Laboratory (LLNL). This sensor has the potential to measure a multitude of trace gases and their isotopologues by choosing a laser tuned to the appropriate wavelengths. Additionally, multiple sample cells could be deployed as an array for improved spatial sampling of fluxes and isotopologues using a single laser source. This decreases the cost and maintenance normally associated with increasing spatial sampling at a site. The sensor is compact and requires low amounts of power through the use of data acquisition units (DAQs) meaning it is ideal for remote in situ deployment or airborne sampling.

We present preliminary tests of the LLNL mini-TDL using a vertical cavity surface-emitting laser (VCSEL) tuned to a narrow spectral range targeting CO₂ absorption lines at 2012 nm. The sample cell is a multi-pass Fraunhofer White cell measuring 5cm x 4cm x 1cm with a total path length of 2.5m. The VCSEL was calibrated in the lab using a Bristol wavelength meter to match CO₂ absorption peaks against the HITRAN 2012 database. We characterize sensor performance in the lab at a range of [CO₂] from 0 ppm to 1000 ppm. Additionally, we show sensor stability under a range of temperature and humidity in an environmental chamber.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-ABS-648409

Predictive Assimilation Framework for Subsurface Process Prediction.

Roelof Versteeg (roelof.versteeg@subsurfaceinsights.com) - Subsurface Insights (PI).

Subsurface system behavior is driven and controlled by the interplay of physical, chemical, and biological processes. These processes occur and are coupled at multiple temporal and spatial scales. The resulting multi-scale, multi process environmental complexity is both an essential attribute of subsurface environments and a major complication in developing an understanding of such environments. The last ten years has seen a rapidly growing appreciation and understanding of the occurrence and importance of these coupled processes and - in parallel with this growing understanding - an increase in the ability to integrate numerical forward and inverse models from different disciplines with heterogeneous datasets (hydrological, geochemical, geophysical, meteorological and microbiological) to provide a holistic understanding of past, current and predicted subsurface system behavior.

Tools for this integration have been developed (and are continuing to be enhanced) by both DOE and university researchers, and are currently applied primarily in the context of research efforts. This application typically involves numerous manual steps in data integration and processing, which are associated with substantial turn-around times between data acquisition and result availability.

There is a substantial value and increasing interest to having this kind of information available for operational efforts, for instance for site remediation and monitoring. This motivated a STTR proposal by Subsurface Insights and Lawrence Berkeley National Laboratory to develop a Predictive Assimilation Framework for subsurface process prediction.

This framework should allow for the automated integration of heterogeneous data with advanced models and the delivery of the resulting information on subsurface processes in near real time in an actionable manner to different stakeholders. This framework is being implemented as a cloud based application. The feasibility of this framework was demonstrated in Phase I of the STTR, and Subsurface Insights was recently selected for the Phase II effort.

In our poster we will discuss the current status and capabilities of this framework as well as the roadmap for framework enhancement in Phase II. The framework is being developed and demonstrated using data from the LBNL Rifle site, and is synergistic with data management and research efforts occurring under the LBNL SFA. Planned enhancements are focused along two thrusts: enhancements of technical capabilities (which have to do with increasing what the framework can do) and enhancements of the underlying software implementation (which has to do with ensuring that the framework can be easily deployed at multiple sites, is robust, and provides for data and result security).

Appendix I: Abstract Poster Session Assignments

Name	Title	Poster#	Room #	Session	Time
Rose Abramoff	Seasonality of C allocation to roots in a mid-latitude forest	106	Room 21	C	Wed 9am
Kristina Anderson-Teixeira	Carbon Dynamics of Forest Recovery under a Changing Climate: Forcings, Feedbacks, and Implications for Earth System Modeling	194	Room 23	C	Wed 9am
Robert Andres	Temporal, Spatial, and Uncertainty Aspects of Carbon Dioxide Emissions from Fossil Fuel Combustion: Highlights of the Last Two Years of TES Funding	1	Room 1	A	Tue 2pm
Dionysios Antonopoulos	Interconnected Cycling of Fe, S, and C in the Terrestrial Subsurface: New Paths and Opportunities for Coupling Biotic and Abiotic Processes	191	Room 23	D	Wed 1030am
Bhavna Arora	Characterizing Biogeochemical Hot Spots and Hot Moments in a Floodplain System	150	Room 21	D	Wed 1030am
Estella Atekwana	Induced Polarization Signature of Biofilms in Porous Media: From Laboratory Experiments to Theoretical Developments and Validation	121	Room 21	A	Tue 2pm
Vanessa Bailey	Pore- to Core-Scale Research to Inform Ecosystem-Scale Soil C Biogeochemistry	203	Room 23	A	Tue 2pm
John Bain	Optimizing ground-penetrating radar for measurement of coarse root biomass and its application in determining elevated CO ₂ legacy effects in an 11-year Florida experiment	162	Room 21	B	Tue 330pm
Dennis Baldocchi	Understanding Interannual Variability of Long Term Flux Measurements over Oak Savanna and Annual Grassland	67	Room 1	B	Tue 330pm
Jillian Banfield	Sustainable Systems SFA 2.0: Extensive genome-resolved analyses reveal roles for uncultivated archaea and bacteria in subsurface biogeochemical cycling	146	Room 21	C	Wed 9am
John Bargar	SLAC SFA: Characterization of uranium and biogeochemical critical elements in organic-rich sediments	231	Room 1	A	Tue 2pm
John Bargar	SLAC SFA: Uranium Biogeochemistry in Organic-Rich Sediments: Laboratory Analog Studies	229	Room 1	C	Wed 9am
John Bargar	SLAC SFA: Coupled cycling of organic matter, uranium, and biogeochemical critical elements in subsurface systems	230	Room 1	D	Wed 1030am
Harry Beller	Chemolithoautotrophy in the Rifle subsurface relevant to C, S, and Fe cycling	147	Room 21	D	Wed 1030am
Keaton Belli	Speciation of uranium controls its kinetics of reduction by metal-reducing bacteria	111	Room 21	A	Tue 2pm
Joe Berry	Solar Induced Fluorescence: Theory and Measurement Approaches	98	Room 20	B	Tue 330pm

Name	Title	Poster#	Room #	Session	Time
Sebastian Biraud	AmeriFlux Management Program QA/QC Technical Team	68	Room 1	B	Tue 330pm
Gautam Bisht	Development of reduced order models to capture subgrid-scale soil moisture dynamics in a polygonal tundra landscape	175	Room 21	B	Tue 330pm
Jeffrey Blanchard	Changes in Soil Microbial Community Structure and Function in a Chronosequence of Warming Experiments at Harvard Forest	154	Room 21	C	Wed 9am
Joel Blum	Isotopic Characterization of Biogeochemical Pools of Mercury and Determination of Reaction Pathways for Mercury Methylation	89	Room 20	C	Wed 9am
Mark Boggs	Microbial Sorption of Plutonium and the Role of Extracellular Polymeric Substances	136	Room 21	D	Wed 1030am
David Bowling	Multi-scale carbon cycle observations and ecosystem process modeling at Niwot Ridge, Colorado	26	Room 1	C	Wed 9am
Maxim Boyanov	Redox dynamics of Hg and U: Mn(II) as a reductant of Hg(II) and the influence of mineral surface sites on the speciation of U(IV)	190	Room 23	B	Tue 330pm
Paul Brooks	Quantifying the role of topographical and edaphic complexity on coupled energy, water, and carbon cycles in forested, montane ecosystems	95	Room 20	A	Tue 2pm
Scott Brooks	Diel mercury-concentration variations in a mercury impacted stream	71	Room 20	D	Wed 1030am
Christopher Brown	Extensive genomic sampling of subsurface microbes provides a new view of the phylogeny and metabolic potential of the bacterial Candidate Phyla OD1 and OP11	105	Room 21	A	Tue 2pm
Edward Brzostek	Towards the development of field methods to characterize environmental controls on rhizosphere priming effects	158	Room 21	B	Tue 330pm
Bill Burgos	Reactivity of Iron-Bearing Phyllosilicates with Uranium and Chromium Through Redox Transition Zones	221	Room 23	C	Wed 9am
Peter Burns	Inorganic Geochemical Controls on Neptunium Transport: Co-Precipitation in Minerals	213	Room 23	D	Wed 1030am
Tony Cahill	Improving Land-Surface Modeling of Evapotranspiration Processes in Tropical Forests	94	Room 20	B	Tue 330pm
Elliott Campbell	Large variability in ecosystem models explains a critical parameter for quantifying GPP with carbonyl sulfide	49	Room 1	D	Wed 1030am
Zoe Cardon	Hydraulic Redistribution of Water Through Plant Roots and Implications for Carbon Cycling and Energy Flux at Multiple Scales	164	Room 21	C	Wed 9am
Jeffrey Catalano	Dominant Mechanisms of Uranium-Phosphate Reactions in Subsurface Sediments	47	Room 1	A	Tue 2pm
Jeffrey Chambers	Controls over biogenic volatile organic compounds from Amazon forests as part of GoAmazon	52	Room 1	B	Tue 330pm
Xingyuan Chen	PNNL SBR SFA: Data Management and Assimilation	46	Room 1	C	Wed 9am

Name	Title	Poster#	Room #	Session	Time
Jon Chorover	Uranium fate in acidic waste-weathered sediments: Scaling of molecular processes to predict reactive transport	48	Room 1	D	Wed 1030am
Cristina Cismasu	Iron and organic matter dynamics under fluctuating redox conditions	144	Room 21	D	Wed 1030am
Aimee Classen	Incorporating Below Ground Biology and Soil Physical Properties into a Soil Carbon Degradation Model through Experimenting Across Ecotypes	163	Room 21	A	Tue 2pm
Mark E. Conrad	Isotopic Evidence for Biogeochemical Interactions Between the Unsaturated Zone and Groundwater in the Rifle Floodplain	142	Room 21	B	Tue 330pm
Nicole DiDonato	Organic Matter Sources in the Speciation and Mobilization of Pu in the Subsurface Environment of the Rocky Flats Site	112	Room 21	C	Wed 9am
Patrick Donovan	Identification of Multiple Mercury Sources to Stream Sediments near Oak Ridge, TN, USA	113	Room 21	D	Wed 1030am
Dan Drell	The DOE Joint Genome Institute--Advancing Energy & Environmental Science	134	Room 21	A	Tue 2pm
Dipankar Dwivedi	Modeling controls on the decomposition of Soil Organic Matter	172	Room 21	B	Tue 330pm
James Ehleringer	Confronting models with regional CO2 observations to improve interpretation of drought stress and emissions (anthropogenic and fire)	31	Room 1	A	Tue 2pm
Dwayne Elias	Organismal and Environmental Level Investigations of the Mercury Methylating Genes hgcAB	73	Room 20	C	Wed 9am
Dwayne Elias	Molecular Biology Level Investigations of the Mercury Methylating Genes hgcAB	75	Room 20	D	Wed 1030am
Scott Fendorf	Subsurface Conditions Controlling Uranium Retention Pathways	223	Room 23	A	Tue 2pm
Scott Fendorf	Spatial Variation in Microbial Processes Controlling Carbon Mineralization within Soils and Sediments	161	Room 21	C	Wed 9am
Marc Flscher	Full-column Greenhouse Gas Profiles Measured at ARM SGP	51	Room 1	B	Tue 330pm
Joshua Fisher	Nutrient Cycle Impacts on Forest Ecosystem Carbon Cycling	193	Room 23	B	Tue 330pm
Charles Flower	Climate change alters woody shrub carbon storage and utilization in a moist acidic tundra	153	Room 21	D	Wed 1030am
David Genereux	Effects of Regional Groundwater on Tropical Rainforest Streams: Carbon Degassing and Particulate Organic Matter	96	Room 20	A	Tue 2pm
Yuri Gorby	Bacterial Nanowires and Extracellular Electron Transfer to Heavy Metals and Radionuclides by Bacterial Isolates from DOE Field Research Centers	207	Room 23	C	Wed 9am
Christopher Gough	Carbon and water cycling following low-severity disturbance in an Upper Great Lakes forest: Empirical and modeling results from an AmeriFlux core site	60	Room 1	C	Wed 9am

Name	Title	Poster#	Room #	Session	Time
David Graham	NGEE Arctic: Biogeochemical controls on microbial CO ₂ and CH ₄ production in polygonal soils from the Barrow Environmental Observatory	181	Room 21	A	Tue 2pm
Natalie Griffiths	Vertical profiles of peat pore water chemistry in a northern peatland reveal dynamic element cycles	3	Room 1	D	Wed 1030am
Lianhong Gu	Lack of explicit representation of mesophyll diffusion explains persistent overestimation of growth rates of historical atmospheric CO ₂ by Earth System Models	10	Room 1	A	Tue 2pm
Baohua Gu	Identification and Quantification of Mercury Binding Functional Groups in Natural Organic Matter and Methylating Bacteria	72	Room 20	B	Tue 330pm
Baohua Gu	Biogeochemical processes affecting Arctic tundra soil organic matter degradation and greenhouse gas emission	182	Room 21	C	Wed 9am
Paul J. Hanson	ORNL's Terrestrial Ecosystem Science Scientific Focus Area - 2014	7	Room 1	B	Tue 330pm
Daniel Hayes	Model-data scaling approaches for assessing the pan-Arctic permafrost carbon feedback	65	Room 1	C	Wed 9am
Terry Hazen	Omics and Geochemistry: the ENIGMA 100-Well Survey	209	Room 23	D	Wed 1030am
Nancy Hess	EMSL: A DOE Scientific User Facility for Terrestrial and Subsurface Science Research	133	Room 21	C	Wed 9am
Ross Hinkle	Carbon Dynamics of the Greater Everglades Watershed and Implications of Climate Change	32	Room 1	D	Wed 1030am
Forrest Hoffman	Representativeness-Based Sampling Network Design and Scaling Strategies for Measurements in Arctic and Tropical Ecosystems	183	Room 21	D	Wed 1030am
Les Hook	ORNL's TES SFA Data and Model Management and Archiving Facilitate Data Sharing and Model-Data Integration	2	Room 1	A	Tue 2pm
Francesca Hopkins	Spatial patterns and source attribution of CH ₄ emissions in an urban airshed to regional/global methane budgets	28	Room 1	B	Tue 330pm
Helen Hsu-Kim	Methods to Quantify Mercury Bioavailability in Sulfidic Sediments	80	Room 20	C	Wed 9am
Maoyi Huang	System Fluxes: Task 1	38	Room 1	C	Wed 9am
Susan Hubbard	The LBNL Sustainable Systems Subsurface Biogeochemistry SFA 2.0: Overview	152	Room 21	A	Tue 2pm
Peter Jaffe	Fate of Uranium During Transport Across the Groundwater-Surface Water Interface	212	Room 23	A	Tue 2pm
Janet Jansson	Impact of fire and natural thaw on permafrost microbial ecology	55	Room 1	D	Wed 1030am
Julie Jastrow	ANL Terrestrial Ecosystem Science SFA: Soil Carbon Response to Environmental Change	131	Room 21	C	Wed 9am

Name	Title	Poster#	Room #	Session	Time
Julie Jastrow	Climatic and edaphic effects on root- and leaf-litter carbon inputs to temperate forest soils	130	Room 21	D	Wed 1030am
Anna Jensen	Drought shifts internal carbon partitioning of recent photosynthates in black spruce trees: From bud to mature shoot	4	Room 1	A	Tue 2pm
Alexander Johs	The Molecular Basis of Mercury Methylation: Expression, Purification and Characterization of HgcA	76	Room 20	D	Wed 1030am
Gabriel Katul	Constraining the simultaneous effects of elevated CO ₂ , temperature, and shifts in rainfall patterns on ecosystem carbon fluxes using multi-scale resource optimization theories	22	Room 1	B	Tue 330pm
Kristina Keating	Integrated geophysical measurements for bioremediation monitoring: combining NMR, magnetic methods and SIP.	122	Room 21	B	Tue 330pm
Ralph Keeling	Large-scale shifts in land metabolic activity indicated by changing seasonal cycle of atmospheric CO ₂	30	Room 1	C	Wed 9am
Ken Kemner	Synchrotron-based characterization of the physical and chemical characteristics of carbon in the subsurface and root zones to improve Earth system modeling of biogeochemical cycling of carbon	189	Room 23	B	Tue 330pm
Annie Kersting	Identifying Molecular Scale Mechanisms Controlling Actinide Transport	135	Room 21	A	Tue 2pm
Terri Killeffer	The NGEA Arctic Data Archive -- Portal for Archiving and Distributing Data and Documentation	184	Room 21	B	Tue 330pm
Eric King	LBNL Sustainable Systems SFA 2.0: Genome-enabled watershed simulation capability (GEWaSC)	149	Room 21	C	Wed 9am
Anthony King	Functional unit testing of the Community Land Model at the PiTS-1 field experiment	11	Room 1	D	Wed 1030am
Sara Knox	Annual balances of CO ₂ and CH ₄ from drained agricultural peatlands and restored wetlands in the Sacramento-San Joaquin Delta, California	107	Room 21	D	Wed 1030am
Joel Kostka	Coupling Peat Decomposition and Metagenomics to Incorporate Molecular Scale Processes into Climate Models	125	Room 21	A	Tue 2pm
Dan Krofcheck	Coupled active and passive remote sensing to describe the land surface of pinon-juniper ecosystems	27	Room 1	A	Tue 2pm
Dan Krofcheck	Investigating the impact of the widespread differential mortality of Pinus-edulus in pinon juniper woodlands: informing remote sensing with eddy-covariance.	108	Room 21	B	Tue 330pm
Lara Kueppers	Responses of subalpine tree recruitment to warming within and above current altitudinal ranges	83	Room 20	A	Tue 2pm
Jitendra Kumar	Multi-scale modeling of hydrologic and biogeochemical processes in Arctic ecosystems	185	Room 21	C	Wed 9am
Beverly Law	The effects of climate, forest age, and disturbance history on carbon and water processes at AmeriFlux sites across gradients in Pacific Northwest forests	29	Room 1	B	Tue 330pm

Name	Title	Poster#	Room #	Session	Time
Jung-Eun Lee	Collaborative Research on Ecophysiological controls on Amazonian precipitation seasonality and variability	100	Room 20	B	Tue 330pm
Anna Liljedahl	Pan-arctic ice wedge degradation in continuous permafrost and hydrological implications	187	Room 21	D	Wed 1030am
Hui Lin	Microbial cell surface interactions and biogeochemical controls on mercury (Hg) redox transformation and methylation	74	Room 20	C	Wed 9am
Chongxuan Liu	Hydro-Biogeochemical Process Dynamics in the Groundwater-Surface Water Interaction Zone: Fundamental Mechanisms and Mechanism-based Models	40	Room 1	C	Wed 9am
Chongxuan Liu	Multiscale Simulations of Hydrological and Biogeochemical Processes from the Pore to Ecosystem Scales	204	Room 23	A	Tue 2pm
Frank Loeffler	Identification of a c-type cytochrome involved in Mn(IV) reduction in Anaeromyxobacter dehalogenans strain 2CP-C	202	Room 23	D	Wed 1030am
Derek Lovley	Going Wireless: Fe(III) Oxide Reduction without Pili by Geobacter sulfurreducens Strain JS-1	200	Room 23	A	Tue 2pm
Derek Lovley	SMART (Subsurface Microbial Activity in Real Time) Technology for Real-Time Monitoring of Subsurface Microbial Metabolism	201	Room 23	B	Tue 330pm
Yiqi Luo	Evaluation and Improvement of Terrestrial Carbon Cycle Models With Observations	196	Room 23	C	Wed 9am
Brian Mailloux	Radiocarbon Signature of Microbial DNA from a Reducing Zone of a Floodplain aquifer, Rifle Colorado	140	Room 21	A	Tue 2pm
Jiafu Mao	Simulation of the Community Land Model in a pine stand with 13CO2 and shading manipulations	8	Room 1	D	Wed 1030am
Matthew Marshall	Multi-System Analysis of Microbial Biofilms	208	Room 23	D	Wed 1030am
Roser Matamala	Differences in Biomass Distribution and Production Budgets between Cropland and Prairie Grassland	132	Room 21	B	Tue 330pm
Melanie Mayes	Microbial dormancy in terrestrial ecosystem models	16	Room 1	A	Tue 2pm
Debapriya Mazumdar	Real-time, on-site and quantitative detection of bioavailable radionuclides and heavy metals in contaminated water at DOE sites	137	Room 21	C	Wed 9am
Nate McDowell	Woodland mortality in a long-term drought experiment	81	Room 20	D	Wed 1030am
Cassandra Medvedeff	Control of Spahgnum-Derived Dissolved Organic Matter on Methane Production in Peatland Soils	197	Room 23	A	Tue 2pm
Jessica Moore	Divergence in how roots and mycorrhizae affect microbial decomposition	109	Room 21	D	Wed 1030am
J William Munger	Fluxes of CO2, CH4, CO, BVOCs, NOx, and O3, in an old growth Amazonian forest	195	Room 23	B	Tue 330pm
Chris Murray	Characteristics of the Hanford Reach of the Columbia River Groundwater-Surface Water Interaction Zone for Investigating Hydro-Biogeochemical Process Dynamics	39	Room 1	B	Tue 330pm

Name	Title	Poster#	Room #	Session	Time
Satish Myneni	Strikingly Different Form of Organic Carbon in Soils of Temperate and Permafrost Soils: Implications for Carbon and Metal Cycling	123	Room 21	A	Tue 2pm
William Nelson	Hydro-Biogeochemical Process Dynamics in the Groundwater-Surface Water Interaction Zone: Macroscopic Processes	41	Room 1	C	Wed 9am
Rebecca Neumann	Methane Oxidation in Boreal Peatlands: A Joint Field, Laboratory and Modeling Investigation	101	Room 20	A	Tue 2pm
Brent Newman	Use of Environmental Tracers for Multi-Scale Investigation of Hydrologic Mixing and Connectivity in the Arctic Coastal Plain, near Barrow, Alaska	177	Room 21	B	Tue 330pm
Peter Nico	Organic-Mineral Dynamics Component of LBNL SFA2.0	145	Room 21	C	Wed 9am
Asko Noormets	Aquaporin-Mediated Reduction in Root Hydraulic Conductivity Impacts Whole Stand Water Use and Carbon Assimilation: Scaling and Modeling the Effect of Sea Level Rise from Roots to the Ecosystem	19	Room 1	D	Wed 1030am
A. Christopher Oishi	Quantifying the interactions between plant water uptake and hydraulic redistribution on the components of evapotranspiration in a mature, unmanaged forest stand	21	Room 1	A	Tue 2pm
Ram Oren	How well do stomatal conductance models perform on closing plant carbon budgets? A test using seedlings grown under current and elevated air temperatures	23	Room 1	B	Tue 330pm
Jessica Osuna	Evaluating the ACASA model as a tool for flux interpretation at 4 AmeriFlux Sites	206	Room 23	C	Wed 9am
Jessica Osuna	Progress toward developing a novel mini tunable diode laser for measuring CO2 fluxes in situ	228	Room 23	D	Wed 1030am
Scott Painter	Status of Ngee-Arctic Track 2 Model Development: Incorporating Dynamic Topography in Fine-scale Models	179	Room 21	A	Tue 2pm
Scott Painter	Three-phase models for thermal hydrology of frozen, variably saturated soils	178	Room 21	D	Wed 1030am
Sari Palmroth	On the complementary relationship between marginal nitrogen and water use efficiencies among Pinus taeda leaves grown under ambient and enriched CO2 environments	24	Room 1	C	Wed 9am
Dario Papale	Connecting ecosystem carbon observatories in Europe and USA -the COOPEUS project and the ICOS infrastructure	66	Room 1	D	Wed 1030am
Anthony Parolari	Modeling complex ecosystem carbon-nitrogen cycle dynamics after disturbance	59	Room 1	A	Tue 2pm
Gilberto Pastorello	AmeriFlux Data Collection, Processing, and Data User Support	69	Room 1	B	Tue 330pm
Jennifer Pett-Ridge	Functioning of wetlands as a source of atmospheric methane: a multi-scale and multi-disciplinary approach at SPRUCE	205	Room 23	A	Tue 2pm
Scott Pitz	Methane Emissions from Upland Trees	102	Room 20	B	Tue 330pm

Name	Title	Poster#	Room #	Session	Time
Brian Powell	Development of a Self-Consistent Model of Plutonium Sorption: Quantification of Sorption Enthalpy and Ligand-Promoted Dissolution	138	Room 21	B	Tue 330pm
Caitlin Pries	The effects of whole profile soil warming on decomposition of native soil carbon and ¹³ C-labeled root inputs	54	Room 1	C	Wed 9am
Sasha Reed	Climate feedbacks in drylands: linking carbon cycling and energy balance above- and belowground	156	Room 21	C	Wed 9am
John Reinfelder	Using mercury-resistant bacteria to examine the effects of thiol complexation and thiol and Mer transporters on the microbial bioavailability of inorganic Hg and methylmercury	93	Room 20	C	Wed 9am
Heidi Renninger	Effects of disturbance on carbon sequestration in the New Jersey Pine Barrens	198	Room 23	B	Tue 330pm
Sigrid Resh	Interactive effects of climate change and decomposer communities on the stabilization of wood-derived carbon in soils: Catalyst for a new study	160	Room 21	D	Wed 1030am
Daniel Ricciuto	Modeling the Hydrological dynamics of the SPRUCE S1 Bog	12	Room 1	D	Wed 1030am
Eric Roden	Geochemical and microbiological response to oxidant introduction into reduced Hanford 300 Area sediments	42	Room 1	A	Tue 2pm
Alistair Rogers	Photosynthesis, Earth System Models and the Arctic	174	Room 21	A	Tue 2pm
Kevin Rosso	Redox Transition Zone Phyllosilicate Reactivity: Thermodynamics and Microscopic Processes	43	Room 1	B	Tue 330pm
Joel Rowland	The role of lateral transport on storage and fate of soil carbon in permafrost dominated hillslopes and hollows.	180	Room 21	B	Tue 330pm
Leilei Ruan	Determining the Drivers of Redox Sensitive Biogeochemistry in Humid Tropical Forests	170	Room 21	C	Wed 9am
Scott Saleska	Tower-mounted cameras validate remotely sensed "green-up" of Amazon forest photosynthesis and reveal mechanisms underlying the seasonality of tropical forest metabolism	103	Room 20	A	Tue 2pm
Scott Saleska	Isotopic Partitioning of CO ₂ fluxes revises understanding of mechanisms of forest carbon sequestration	99	Room 20	D	Wed 1030am
Peter H. Santschi	Plutonium Immobilization and Mobilization by Soil Organic Matter	215	Room 23	C	Wed 9am
Peter H. Santschi	Collaborative Research: The Importance of Organo-Iodine and Iodate in Iodine-127,129 Speciation, Mobility, and Microbial Activity in Groundwater at DOE Sites	217	Room 23	D	Wed 1030am
Kathleen Savage	Partitioning Autotrophic and Heterotrophic Contributions to Soil Respiration: A Tale of Two Trenches	104	Room 20	B	Tue 330pm
Christopher Schadt	Scoping potential microbial responses to warming and drying in the SPRUCE peatland ecosystem.	5	Room 1	C	Wed 9am
Jeffra Schaefer	A comparison of Hg(II) uptake and accumulation between mercury methylating and non-methylating bacteria	92	Room 20	C	Wed 9am

Name	Title	Poster#	Room #	Session	Time
Michael Schaefer	Variation in Microbial Processes Controlling Carbon Mineralization within Wetland Soils	110	Room 21	D	Wed 1030am
Timothy Scheibe	Multiscale Science and Modeling: Task 4	45	Room 1	D	Wed 1030am
Michelle Scherer	Electron Transfer and Atom Exchange Between Fe(II) and Structural Fe(III) in Clays	192	Room 23	A	Tue 2pm
Ted Schuur	The Impact of Permafrost Carbon Loss on the Carbon Balance of an Experimentally Warmed Tundra Ecosystem	123	Room 21	A	Tue 2pm
Sanna Sevanto	Differences in hydraulic strategy show in plant responses to heat and drought treatments	82	Room 20	D	Wed 1030am
Jonathan (Josh) Sharp	Geochemical zonation linked to microbial spatial distribution and microbe-mineral interactions in metal-immobilizing systems	225	Room 23	B	Tue 330pm
Liang Shi	Microbial Extracellular Electron Transfer Mechanism in Hanford Subsurface Geobacter spp.	44	Room 1	A	Tue 2pm
Alyssa Shiel	²³⁸ U/ ²³⁵ U as an indicator of re-oxidation of U(IV) in the subsurface of remediated sites	219	Room 23	C	Wed 9am
Julie Shoemaker	Multi-scale methane fluxes from Howland Forest: merging tower and chamber flux measurements.	25	Room 1	B	Tue 330pm
Jeremy Smith	Determining Mechanisms of Hg Methylation by HgcA and intramolecular Hg transfer by MerA at the Atomic Scale	78	Room 20	A	Tue 2pm
Lydia Smith	Radiocarbon measurements to assess soil carbon vulnerability in Arctic coastal tundra	186	Room 21	B	Tue 330pm
Anne Summers	Identifying Components of Toxic Metal Stress and Hg Methylation with Global Proteomics	90	Room 20	B	Tue 330pm
Martial Taillefert	Mineral Solubility and Free Energy Controls on Microbial Reaction Kinetics: Application to Contaminant Transport in the Subsurface	227	Room 23	D	Wed 1030am
Jianwu Tang	Physiological controls of stem respiration and soil respiration in a temperate forest	159	Room 21	C	Wed 9am
Neslihan Tas	Metagenomics and microbial community profiling across polygon features at the Next Generation Ecosystem Experiment (NGEE)-Arctic Barrow site	176	Room 21	D	Wed 1030am
Nishanth Tharayil	Developing surface-modified polymeric probes for the in-situ capture of plant root exudates	157	Room 21	A	Tue 2pm
Ming Tien	Survival During Long Term Starvation: Global Proteomics Analysis of Geobacter sulfurreducens Under Prolong Electron Acceptor and Donor Limitation	210	Room 23	A	Tue 2pm
Tetsu Tokunaga	Water and carbon fluxes into groundwater from a semi-arid floodplain vadose zone	143	Room 21	B	Tue 330pm
Margaret Torn	LBNL Terrestrial Ecosystem Science SFA: Belowground carbon cycling	53	Room 1	B	Tue 330pm
Margaret Torn	The AmeriFlux Management Project: Overview	70	Room 1	C	Wed 9am

Name	Title	Poster#	Room #	Session	Time
Amy Trowbridge	Up-rooting surface-atmosphere exchange models: How mycorrhizal associations may affect soil emission profiles	97	Room 20	C	Wed 9am
Albert Valocchi	Pore-Scale and Continuum Simulation of Microfluidics Experiments on Reactive Transport and Multiphase Flow conducted at EMSL	117	Room 21	C	Wed 9am
Albert Valocchi	Microbiological-enhanced mixing across scales during in-situ bioreduction of metals and radionuclides at Department of Energy Sites	119	Room 21	D	Wed 1030am
Kees Jan van Groenigen	A New Approach to Synthesizing Results from Global Change Experiments	18	Room 1	D	Wed 1030am
Charuleka Varadharajan	Sustainable Systems SFA Data Management and Assimilation	141	Room 21	A	Tue 2pm
Roelof Versteeg	Predictive Assimilation Framework for Subsurface Process Prediction.	139	Room 21	B	Tue 330pm
Anthony Walker	Vegetation turnover and nitrogen feedback drive temperate forest carbon sequestration in response to elevated CO ₂ . A multi-model analysis.	15	Room 1	A	Tue 2pm
Matthew Wallenstein	Advancing our understanding of carbon-climate feedbacks in Arctic tundra: litter input controls on soil organic matter turnover and formation	171	Room 21	C	Wed 9am
Gangsheng Wang	Microbial dormancy in terrestrial ecosystem models	9	Room 1	B	Tue 330pm
Dali Wang	Experiment-Inspired Software Design and Ecosystem Modular Testing for CLM Development	13	Room 1	C	Wed 9am
Li Wang	Illite spatial distribution regulates Cr(VI) adsorption capacity and kinetics	114	Room 21	D	Wed 1030am
Scott Wankel	15N and 18O isotope systematics of anaerobic abiotic reduction of nitrite by iron (II)	211	Room 23	B	Tue 330pm
Eric Ward	Partitioning Ecosystem Canopy Transpiration to Evaluate the Sensitivity Stomatal Conductance to Changing Climate Indicators.	20	Room 1	D	Wed 1030am
Jeff Warren	Plant water relations in an ombrotrophic bog (SPRUCE S1) partitioning water use and stress tolerance among components	6	Room 1	A	Tue 2pm
David Watson	Capturing Transient Climate-Driven Contributions of Surface to Subsurface Processes at Watershed Scales	77	Room 20	D	Wed 1030am
Kenneth Williams	Floodplains as biogeochemical reactors: Using multi-scale approaches to quantify hot spots and hot moments at DOE's Rifle, Colorado field site	151	Room 21	A	Tue 2pm
David Williams	The Prairie Heating and CO ₂ Enrichment (PHACE) experiment: Synthesizing 8 years of data	155	Room 21	B	Tue 330pm
Weimin Wu	Long-term uranium sequestration as nitrate invades a previously reduced zone - DOE Oak Ridge IFRC site	79	Room 20	A	Tue 2pm

Name	Title	Poster#	Room #	Session	Time
Yuxin Wu	Multi-scale Geophysical Studies at the NGEE-Arctic Site	173	Room 21	C	Wed 9am
Stan Wullschleger	Characterizing rooting depth distribution and nitrogen acquisition by dominant tundra plant species	188	Room 21	D	Wed 1030am
Xiaofeng Xu	Integrating In-situ Data with a Model for Examining Community-level CO ₂ and CH ₄ flux in a Carbon-rich Peatland in Northern Minnesota	17	Room 1	B	Tue 330pm
Steve Yabusaki	Seasonal Hydrology and Biogeochemical Hot Spots: Carbon, Nitrogen and Mineralogic Controls on Suboxic Conditions in the Rifle Floodplain Aquifer	148	Room 21	A	Tue 2pm
Xiaojuan Yang	Nutrient regulation of tropical ecosystem responses to environmental changes: a case study in the Amazon region	14	Room 1	C	Wed 9am
Fan Yang	The Genetic Potential of Microbial Depolymerization of SPRUCE Peatland in Marcell Experimental Forest, MN	61	Room 1	D	Wed 1030am
Ming Ye	Computational Bayesian Framework for Quantification and Reduction of Predictive Uncertainty in Groundwater Reactive Transport Modeling	116	Room 21	B	Tue 330pm
Nathan Yee	Hg(0) Oxidation by Anaerobic Bacteria	91	Room 20	B	Tue 330pm
John Zachara	Pacific Northwest National Laboratory SFA: Hydro-Biogeochemical Process Dynamics in the Groundwater-Surface Water Interaction Zone	37	Room 1	A	Tue 2pm

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